A STUDY OF THE EFFECTS OF CHLORINATION AND CAUSTIC EXTRACTION ON THE CARBOHYDRATE FRACTION OF AN ASPEN NEUTRAL SULFITE SEMICHEMICAL PULP

A thesis submitted by

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in partial fulfillment of the requirements
of The Institute of Paper Chemistry
for the degree of Doctor of Philosophy
from Lawrence College,
Appleton, Wisconsin

June, 1955

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GLOSSARY

Acid system--developing solution used in paper chromatography consisting of 9 parts ethyl acetate, 2 parts glacial acetic acid and 2 parts water (page 7).

Alkali-resistant cellulose--the fibrous residue remaining after the extraction of hemicelluloses from holocellulose (page 18).

Amberlite IR-4B(OA_c) anion resin--the parenthetical term used with the name of the anion resin denotes the condition of the resin, that is, that it was regenerated with acetic acid. Hydroxide (OH) and carbonate (CO_3) forms were also used (page 10).

Glucan, Xylan, etc.--these terms represent calculated values of polysaccharides determined from the simple sugars in the various hydrolyzates. It is used only as a means of expressing data and should not be interpreted as representing a specific component of the various materials studied.

Hemicelluloses--the material extracted from holocellulose successively with 5 and 16% potassium hydroxide, which precipitated in alcohol (page 18).

Holocellulose--holocellulose as isolated by a modified Wethern technique (page 17).

Klason lignin--the insoluble residue from the standard 72% sulfuric acid method for determining lignin (page 16).

Maule test-- qualitative test for hardwood lignin (syringyl grouping). A purple color results when chlorinated lignin is treated with ammonia (22).

Molisch test--qualitative test for carbohydrates. A purple ring forms at the interface when sulfuric acid is allowed to flow into a mixture of the carbohydrate in a 10% solution of alpha-napthol in chloroform (27).

Pentosans-- pentosan content as determined in the pulps by the formation of furfural in 12% hydrochloric acid (page 17).

Polyuronide (uronic acid content)--polyuronides as determined on the pulps by carbon dioxide evolution (page 17).

Pyridine system--developing solution used in paper chromatography consisting of 3 parts pyridine, 10 parts butanol and 3 parts water (page 7).

Soluble lignin--the lignin soluble in the filtrates from the Klason lignin determination as measured by the ultraviolet absorption of the filtrates (page 24).

INTRODUCTION

Neutral sulfite semichemical pulps can be bleached in a single stage with peroxides and hypochlorites to a brightness of 70 to 75 with only small losses in yield (1 to 4%). Using a multistage bleaching sequence (i.e., chlorination, caustic extraction, and hypochlorite oxidation) brightnesses of 80 to 85 are possible and the strength properties are markedly improved. However, 15 to 20% of the pulp is lost thereby reducing the yield based on the original wood to about 60%. Since high yields are a major feature in neutral sulfite semichemical pulping, the attack on the various components of the pulp in bleaching is of great interest. A fundamental knowledge of the effect of bleaching on the carbohydrate fraction in particular would be of value in determining an economic balance between cooking and bleaching for pulp preparation and also in preparing specific types of pulp.

The work described in this thesis has been restricted to the effect of the chlorination and caustic extraction stages of bleaching on the carbohydrate fraction of a neutral sulfite semichemical pulp. The literature on this subject for either semichemical or chemical pulps is limited.

Hägglund (1) stated that in the multistage bleaching of sulfite and sulfate pulps, the higher the lignin content the greater will be the loss of hemicelluloses. It was determined that this loss was not the result of hydrolysis by the hydrochloric acid formed in the chlorination stage. Although lengthy and repeated chlorinations increased the alkali solubility of isolated polysaccharides, Hägglund

did not believe that the carbohydrate fraction in pulp was attacked in the chlorination stage because the chlorine concentration is low and because the chlorine is rapidly consumed by the lignin. The yields and alpha-cellulose contents of bleached sulfite and sulfate pulps were found to be independent of the cooking degree of the unbleached pulp. On the basis of these observations, Hägglund suggested that soluble hemicelluloses were split from lignin by the chlorination reaction.

Norman and Shrikhande (2) also suggested that chlorination split a bond between lignin and carbohydrates. They found that polyuronides and lignin could be more easily removed from plant materials with sodium sulfite after chlorination.

Larson (3) found that lignin was the only product removed during chlorination of a normal sulfite pulp. However, with a rawer pulp, a considerable amount of carbohydrate material was removed (2 to 4% of the unbleached pulp). The greater the amount of chlorine used the greater the quantity of carbohydrates dissolved. In the caustic extraction stage, Larson found that the amount of reducing material in the spent liquor, calculated as glucose, was 3 to 50% of the amount of lignin removed depending on the condition of extraction. The ratio of carbohydrates to lignin removed by caustic extraction was greater for pulps of low lignin content than for rawer pulps.

Loeschbrandt (4) studied the bleaching of sulfate pulps. In the spent liquors from the caustic extraction stage, he found a

fraction which he postulated was hemicellulosic material. The magnitude of this fraction increased with the amount of chlorine used in the chlorination stage and with the pH and temperature of the caustic extraction. After a second chlorination and caustic extraction, the proportion of this fraction in the spent caustic extraction liquor increased. However, the carbohydrates were not experimentally identified or measured.

Trivedi, Kingsbury, and Simmonds (5) found an apparent loss of 4.4% (unbleached pulp basis) of carbohydrate material during the chlorination of a neutral sulfite semichemical pulp. This value was determined from the difference between the total material removed and the lignin removed (calculated as the difference between lignin contents of the unbleached and chlorinated pulps). The alpha-cellulose content was constant. The loss of carbohydrates during chlorination was greater than the combined carbohydrate losses in the following caustic extraction and hypochlorite stages. It was postulated that the chlorination of lignin released water-soluble hemicelluloses. The loss of carbohydrate material in the caustic extraction stage ranged from 1.7 to 5.5% (unbleached pulp basis) depending on the temperature and the concentration of sodium hydroxide. The alpha-cellulose content was not reduced during caustic extraction until the temperature was above 70°C. or the caustic concentration was about 3.5%.

Dyfverman, Lindberg, and Wood (6) and Lindberg and Wood (7) have studied the chlorine oxidation of methyl glycosides of glucose, galactose, mannose, and xylose. These glycosides were slowly oxidized

to aldonic acids and the aldonic acids were further oxidized to keto-acids or dibasic acids. Apparently, the reaction did not proceed by way of an initial hydrolysis of the glycoside followed by oxidation but the oxidation probably proceeded by way of a chloroderivative. Dyfverman (8) also studied the chlorine oxidation of methyl cellobioside and found that the first product formed was cellobionic acid. Gluconic acid as well as smaller amounts of other acids formed later in the reaction.

Björkqvist, Gustafsson, and Jörgensen (9) studied the loss of carbohydrates during the chlorination and hypochlorite oxidation of birch and spruce neutral sulfite semichemical pulps by measuring the simple sugar composition of the hydrolyzates of the pulp residues. For the birch pulp, they found that the carbohydrate losses during chlorination occurred only in what they called the noncellulosic hexosans, which included mannose, galactose and the glucose which does not originate in the cellulose. There was no change in the absolute amounts of pentosans or uronic acids. A total loss of carbohydrates of 1 to 4% (unbleached pulp basis) depending on the severity of the chlorination was indicated. The spruce pulp, in contrast to the birch pulp, retained some of the noncellulosic hexosans during chlorination but lost some pentosans.

PRESENTATION OF THE PROBLEM

It was proposed to study some of the effects of chlorination and caustic extraction on the carbohydrate fraction of an aspen neutral sulfite semichemical pulp. The problem was approached in two ways: (a) the carbohydrate components of the pulp residues were characterized, and (b) the carbohydrate components of the spent liquors were isolated and were described in terms of the yield and the simple sugar composition after hydrolysis. The yields of lignin in the pulp residues and in the spent liquors were determined in an effort to obtain a material balance.

EXPERIMENTAL PROCEDURES AND ANALYTICAL METHODS

GENERAL PROCEDURES FOR THE ANALYSIS OF SUGARS

QUALITATIVE ANALYSIS OF SUGAR SOLUTIONS

The chromatograms were prepared as shown in Figure 1. Whatman No. 1 filter paper was used.

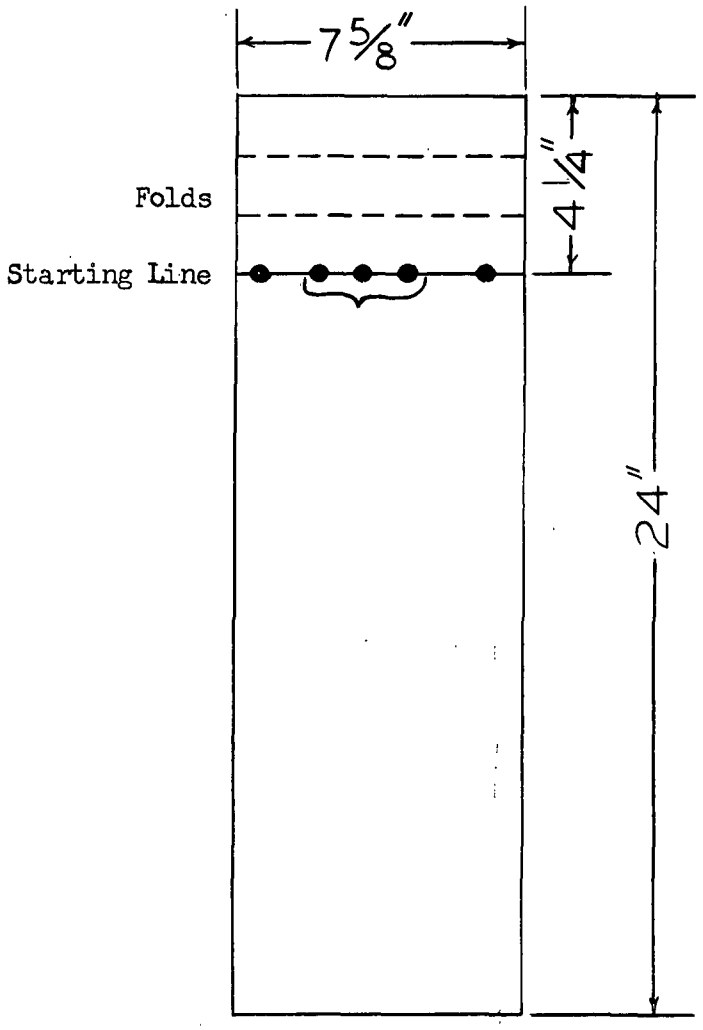

Figure 1. Preparation of Chromatograms

The chromatograms were developed with a solution of ethyl acetate, glacial acetic acid, and water (9:2:2) for 24 to 35 hours or with a solution of pyridine, butanol, and water (3:10:3) for 48 hours. The first will be designated as the acid system and the second as the pyridine system. The acid system solvent was freshly prepared for each chromatogram.

The developed chromatograms were air dried and then sprayed with aniline hydrogen phthalate spray reagent which consisted of 9.3 g. aniline, 14.8 g. phthalic acid anhydride, 845 ml. butanol, and 155 ml. water. After heating the sprayed chromatograms at 100-125°C. for several minutes, colored spots indicating the location of the sugars became visible. Ultraviolet light was used to find trace amounts of sugar after spraying with aniline hydrogen phthalate and heating.

QUANTITATIVE ANALYSIS OF SUGAR SOLUTIONS

The simple sugar components in a solution were determined by the method of Hirst and Jones (10). The sugars, isolated by paper chromatography, were oxidized to formic acid with sodium periodate and then the amount of formic acid was measured. The ratio of the formic acid from the unknown sugar to that from a known amount of ribose which had been added to the solution was used to calculate the amount of unknown sugar present.* The details of the procedure are given on the following page.

*No ribose was detected in any of the pulp residues or liquor fractions.

A continuous, narrow band of the sugar solution was placed along the starting line to within 3/4 inches of each side. The chromatograms were either developed in the pyridine system for a series of 48, 24, and 24 hours with intermediate air drying or for 35 hours in the acid system followed with 24 hours in the pyridine system after air drying. The first sequence gave a good separation of galactose and glucose and the second sequence gave a good separation of xylose and ribose.

After the chromatograms were developed, a strip 1.5 inches wide was cut from each side and sprayed with aniline hydrogen phthalate to locate the positions of the sugars. Ultraviolet light was used to find the extremities of the sugar positions. These guide strips were reattached to the chromatogram and the areas of the isolated sugars were marked and cut from the unsprayed portions of the chromatogram. The sugar was eluted from the paper with distilled water as shown in Figure 2. The water, carrying the sugar, dripped into a 38 by 200--mm.

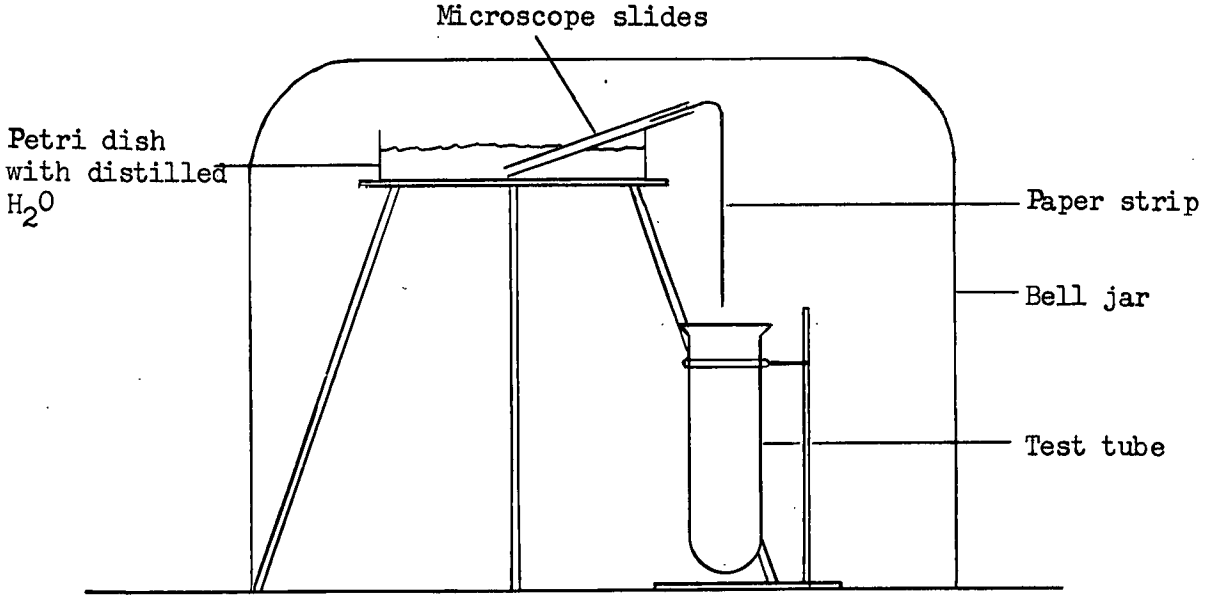

Figure 2. Elution of Isolated Sugars

Pyrex test tube. The strips were eluted a minimum of 2-1/2 hours. The eluted strips were air dried and sprayed with aniline hydrogen phthalate to check the completeness of elution.

One milliliter of approximately 0.25 N sodium periodate was added to the eluted sugar in the test tube. If more than 3.5 mg. of sugar were present, additional sodium periodate was used. The sides of the test tube were washed down with 5 ml. distilled water. The test tube was covered with a no. 29 Pyrex stopper held in place with rubber bands. The lower part of the test tube containing the solution was put in boiling water for 20 minutes and then cooled in cold water. Then, 0.5 ml. of technical ethylene glycol was added to consume the excess sodium periodate, the stopper and sides of the test tube were rinsed with distilled water and the mixture was allowed to stand 10 minutes. The solution was titrated to a methyl red end point with approximately 0.0025 N sodium hydroxide. If it was extimated that more than 20 ml. of the dilute base were required, a stronger alkaline solution of known relative strength was used in order to obtain a sharper end point.

The chromatogram paper itself had a titration value. Therefore, a paper blank was determined from strips cut from each chromatogram, both above and below the location of the sugars. The titration values were corrected for the average of these blanks or for the blank located nearest to the sugar areas on the chromatogram provided there was an appreciable difference in blanks taken from the top and bottom. The correction for the blank included a correction for the relative areas of the strip containing the sugar and the strip used for the blank.

In the sodium periodate oxidation, one mole of hexose sugar yields five moles of formic acid, one mole of pentose sugar yields four moles of formic acid, and one mole of methyl pentose sugar (rhamnose) yields four moles of formic acid. The amount of sugar in the sample was thus calculated as follows:

$$\text{Weight hexose} = \text{weight ribose in sample} \times \frac{\text{titration hexose}}{1.0413 \times \text{titration ribose}}$$

$$\text{Weight pentose} = \text{weight ribose in sample} \times \frac{\text{titration pentose}}{\text{titration ribose}}$$

$$\text{Weight rhamnose} = \text{weight ribose in sample} \times \frac{1.2633 \text{ titration rhamnose}}{1.0413 \text{ titration ribose}}$$

GENERAL PROCEDURES FOR THE USE OF ION EXCHANGE RESINS

The first step in conditioning new cation and anion resins was to wash them free of fines by alternately suspending the resin in tap water and decanting the supernatant liquor. The washed resins were treated alternately batchwise with 1 N hydrochloric acid and 0.5 N sodium hydroxide six times. Then the resins were placed in large Buchner funnels. The cation resin was regenerated with 1 N hydrochloric aced and the anion resin was regenerated with 0.5 N sodium hydroxide. Finally, the cation resin was washed free of the chloride ion and the anion resin was washed until the effluent was neutral to alkacid paper. These resins were kept moist and were used as the stock supply of resin.

Generally the anion resin was converted to the carbonate form ($CO_3^=$) with 2% sodium carbonate or to the acetate form (OAc^-) with 1 N acetic acid before using with sugar solutions.

Columns were packed by pouring a water suspension of resin into the column which was filled with water. The excess water drained from the bottom of the column. This resulted in a uniformly packed column with no entrained air. The columns were thoroughly washed before using.

Material retained by the anion column was recovered by elution with sulfuric acid (pH 1.0 to 1.5). All of the solutions encountered in this study contained chloride ions. The elution was continued through the chloride ion break-through and the sulfate ion break-through until the chloride ion could no longer be detected with silver nitrate.

When a large quantity of used resin had been collected, it was regenerated as described above.

PREPARATION OF UNBLEACHED AND BLEACHED PULPS AND SPENT BLEACH LIQUORS

PREPARATION OF UNBLEACHED PULP

A small log of about twenty pounds was taken from each of four aspen trees (Populus tremuloides) cut near Appleton, Wisconsin in December, 1953. A comparison of the logs is shown in Table I.

TABLE I

AGE, GROWTH RATE AND SPECIFIC GRAVITY OF THE ASPEN WOOD

	Log A	Log B	Log C	Log D
Age, yrs.	20	38	36	38
Av. no. of rings/inch	9	15	10	10
Specific gravity (dry wood basis)	0.41	0.44	0.46	0.44

The logs were peeled and then chipped in a 36 in., two-knife chipper set to cut a nominal 3/4-in. chip. The chips from the four logs were combined and screened. The moisture content of the combined chips was 53.7%.

A stationary, indirect-heated, stainless steel digester of 44-liter capacity was used for cooking. The chips were held in a stainless steel basket that fitted inside the digester. When a temperature of 100°C. was reached, the digester was relieved to zero pressure. At the end of the cook, the pressure was relieved over a period of 15 minutes. The cooked chips, while still hot, were defibered in a commercial size Bauer refiner. The clearance of the refiner plates was set at 0.008 in.

The pulps were washed in a muslin-covered washbox, centrifuged to a moisture content of about 75% and then stored at 5°C. Four batches of pulp were made to demonstrate reproducibility. The four pulps were resuspended in water, combined, air dried, and stored in Pliofilm bags.

PRETREATMENT OF UNBLEACHED PULP

The airdry, unbleached pulp was soaked in water in preparation for all reactions. The pulp was covered with 1200 ml. distilled water per 100 g. airdry pulp and kept at 8°C. for 19 hours. The slurry was then filtered by suction on a Buchner funnel through a double layer of Cenco No. 13260 filter paper and washed with 1 liter of distilled water.

PREPARATION OF CHLORINATED PULPS

The unbleached pulp samples were chlorinated in a stoppered bottle. Chlorine was added as chlorine water. Temperature was controlled by use of a water bath. The pulp slurry was agitated by swirling in the bottle manually in all chlorinations except chlorination 3 for which a Lightnin' mixer was used. The slurries were agitated almost continuously in the first five minutes of chlorination and thereafter about once every five minutes.

Chlorination was allowed to continue for the time periods indicated in Table IX. In this sample, excess chlorine was consumed by adding a small amount of sulfurous acid. The other chlorinations were allowed to continue until the chlorine was exhausted as indicated by starch-iodide test paper. At the end of the reaction, the pulp slurry was immediately filtered by suction on a Buchner funnel through a double layer of Cenco No. 13260 filter paper. The pulp was washed by alternately soaking in distilled water and filtering until the washings were colorless and neutral to blue litmus and alkacid paper. The liquors were treated as described on page 59.

The portion of the chlorinated pulp used for the holocellulose preparation was not air dried. The remainder of the pulp was air dried for the other analyses.

PREPARATION OF CAUSTIC-EXTRACTED PULPS

The caustic extractions were carried out in beakers. The pulp and liquor were brought to temperature before mixing. Mixing of the high consistency mixture was accomplished by kneading by hand protected with a rubber glove.

After sixty minutes, the pulp mixture was filtered by suction through a double layer of Cenco No. 13260 filter paper. The pulp was washed repeatedly by suspending it in distilled water and filtering as above until the washings were colorless and neutral to litmus paper. The liquors were treated as described on page 67.

The portion of the caustic-extracted pulp used for the holocellulose preparation was not dried. The remainder of the pulp was air dried for the other analyses.

PREPARATION OF HYPOCHLORITE-TREATED PULPS

Samples of the composite caustic-extracted pulps were treated with calcium hypochlorite to determine the final brightness which could be obtained. The samples were bleached at 2% consistency and 45°C. with 0.5, 1.5, 3.0, 4.0, and 6.0% available chlorine as hypochlorite. All of the available chlorine was consumed in the first three samples as indicated by starch-iodide paper. The last two samples were allowed to react 3 hours. Brightness handsheets were made according to Institute Method 412 (1951).

ANALYSIS OF PULP RESIDUES

DETERMINATION OF THE OVENDRY CONTENT

The ovendry content of pulp residues was determined at the same time that samples were taken for any determination or reaction with the exception of lignin, pentosan, uronic acid and ash determinations. The pulp was mixed thoroughly and spread out on a table. Small amounts taken randomly throughout the pulp were placed in tared glass weighing bottles and either dried overnight (16 hrs.) or to constant weight at 103 to 105°C.

For the determination of pentosans, lignin, uronic acids and ash, a supply of pulp which had been ground in an Abbe Mill was stored in a closed bottle for one week. Then, the ovendry content was determined, and this value was used for all the tests made on these pulp samples. All tests were made within one week after the ovendry content had been determined.

In all cases, the value for the ovendry content was an average of four determinations.

DETERMINATION OF ASH

The ash was determined as sulfated ash according to Institute Method 712 (1947).

It was assumed that the ash was present as salts of acidic groupings in the pulp. The ash of the unbleached pulp, chlorinated pulp, holocellulose from unbleached pulp and holocellulose from chlorinated pulp was calculated as an equal mixture of metallic

calcium and sodium. The ash of the alkali-resistant celluloses and hemicelluloses was calculated as potassium. The sulfated ash of the hemicelluloses was found to be water soluble and it was assumed that this was potassium sulfate.

DETERMINATION OF KLASON LIGNIN

The Klason lignin content was determined according to Institute Method 428 with the exception that the boiling 3% acid stage was carried out under reflux instead of in an open beaker.

The product will be designated as Klason lignin in this thesis to emphasize that it was the result of a method of determination and not necessarily a chemical entity.

DETERMINATION OF SOLUBLE LIGNIN

The amount of lignin remaining dissolved in the filtrates from the Klason lignin determination was estimated from the ultraviolet absorbance of the solution. This method is discussed in detail on page 23.

DETERMINATION OF ALCOHOL-SOLUBLE MATERIAL

The material extracted by 95% ethyl alcohol in pre-extracting the pulp samples for the Klason lignin determination was determined according to Institute Method 24 (1951).

DETERMINATION OF NITROGEN CONTENT

The nitrogen content was determined by the analytical laboratory according to Institute Method 606 (1951). Boric acid was used for absorbing the ammonia.

DETERMINATION OF PENTOSANS

Institute Method 424 (1951) was used. The following factor was subtracted from the pentosan value determined by this method in order to correct for the furfural contribution from uronic acids.

$$\frac{\%\ \text{uronic anhydride}}{4} \times \frac{\text{M.W. furfural}}{\text{M.W. } CO_2} \times \frac{\text{M.W. pentosans}}{\text{M.W. furfural}} \times 0.35$$

DETERMINATION OF POLYURONIDES

Institute Method 25 (1951) was used.

PREPARATION OF HOLOCELLULOSE

The holocellulose preparation was a modification of that developed by Thomas (11) and Wethern (12). Details of the procedure are as follows:

1. The chlorinating solution (carbon tetrachloride saturated with chlorine and cooled to -5°C. was added to moist pulp which was cooled below 5°C. (ten ml. of chlorinating solution per gram of pulp).
2. The above slurry was continuously stirred for five minutes in an ice-alcohol bath.
3. The mixture was filtered by suction on a fritted glass Buchner funnel.

4. The following extractions were made on the funnel:

   a. cold (10°C.) 3% solution of ethanolamine in absolute alcohol (twice)

   b. hot (75°C.) ethanolamine solution (twice)

   c. soaked with hot ethanolamine solution for two minutes

   d. steps a to c repeated

   e. cold absolute alcohol

   f. cold 50% alcohol

5. Steps 1 to 4 were repeated twice. However, the chlorination time was reduced to three minutes. Step 4-f was a preparatory step necessary only prior to a chlorination.

6. The pulp was finally washed with acetone and air dried.

PREPARATION OF ALKALI-RESISTANT CELLULOSE AND HEMICELLULOSES (13)

About 30 g. of air-dried holocellulose were placed in a 1-liter filter flask. The air was replaced with nitrogen and the temperature of the system was brought to 20°C. Then 600 ml. of 5% potassium hydroxide solution at 20°C. was added. The air was replaced with nitrogen again and the system was maintained at 20°C. in a water bath for two hours with occasional swirling.

At the end of two hours, the mixture was filtered by suction on a coarse porosity, fritted-glass Buchner-type funnel. The liquor was filtered into an excess of concentrated acetic acid. The residue was immediately washed with 150 ml. of 5% potassium hydroxide solution and 150 ml. water. The filtrate with the washings was poured into 4000 ml. of absolute ethyl alcohol and mixed thoroughly. The residue

was washed with 2% acetic acid and then washed with water until neutral to litmus paper. The residue was finally washed with acetone and air dried.

The air-dried residue from the 5% extraction was returned to the 1-liter filter flask and extracted again with a 16% potassium hydroxide solution in the same manner.

The pulp mixture was again filtered by suction with the filtrate going into an excess of concentrated acetic acid. The residue was immediately washed with 80 ml. of 16% potassium hydroxide solution, 80 ml. of 5% potassium hydroxide solution, and 150 ml. water. The filtrate and washings were poured into 4000 ml. of absolute ethyl alcohol and combined with the alcohol mixture from the 5% extraction and allowed to settle 48 hours or more.

The residue was washed with 2% acetic acid and then with water until neutral to litmus paper and finally washed with acetone and air dried. This residue will be designated as alkali-resistant cellulose.

Most of the supernatant alcohol solution was siphoned from the precipitated hemicelluloses. The hemicelluloses were separated from the remainder of the liquor by centrifuging, washed six times with hot ethyl alcohol, three times with ether, and then dried *in vacuo* over calcium chloride and paraffin shavings at 20 to 25°C.

DETERMINATION OF THE SIMPLE SUGAR COMPONENTS OF THE ALKALI-RESISTANT CELLULOSE

The alkali-resistant cellulose was hydrolyzed according to the procedure of Saeman, Bubl and Harris (14) with the exception that the

time of treatment in 72% sulfuric acid was extended from 45 minutes to 60 minutes so as to insure complete solution.

An accurately weighed sample of the alkali-resistant cellulose consisting of 175±1 mg. of each of the duplicate was treated with 5 ml. of 72% sulfuric acid at 30°C. for 60 minutes. The solution was diluted with 140 ml. water to give a 5% acid solution and refluxed 4-1/2 hours.

An accurately weighed amount of ribose (about 70 mg.) was added to the hydrolyzate, which was then neutralized to a pH of about 6.0 with a saturated barium hydroxide solution. The barium sulfate was removed by filtering through a celite pad. The filtrate was passed through an Amberlite IR-120 cation exchange column and then concentrated *in vacuo* at 22°C. to about 5 ml.

The simple sugars in the hydrolyzate were separated by chromatography and determined quantitatively.

DETERMINATION OF THE SIMPLE SUGAR COMPONENTS OF THE HEMICELLULOSES

An accurately weighed sample of hemicellulose consisting of 100±1 mg. of each of the duplicate samples was treated with 2 ml. of 72% sulfuric acid at 10°C. for 30 minutes. The solution was then diluted with 116 ml. distilled water to give a 2% acid solution. The dilute acid solution was refluxed three hours, inasmuch as it had been experimentally determined that this time gave maximum reducing values.

After refluxing, the sample was cooled and an accurately weighed amount of ribose (about 80 mg.) was added. The pH of the solution was

adjusted to 6.0-6.3 with a saturated barium hydroxide solution. The barium sulfate was removed by filtering through a celite bed. The neutralized solution was passed through an Amberlite IR-120 cation exchange column and concentrated in vacuo at 22°C. to about 4 ml.

The simple sugars in the concentrated hydrolyzate were separated by chromatography and determined quantitatively.

ANALYSIS OF SPENT LIQUOR FRACTIONS

FRACTIONATION OF THE SPENT LIQUORS

The procedures for fractionating the spent liquors are given on pages 59 to 62 and 67 to 70.

SOLIDS CONTENT OF FRACTIONS ISOLATED AS FOLUTIONS

The sample was evaporated to dryness on a steam bath in a tared weighing bottle. In the case of ether or dioxane solutions, the sample was only concentrated to a small volume on the steam bath and then evaporated to dryness at room temperature in vacuo. The samples were heated at 60°C. in vacuo for 0.5-hour intervals until a constant weight or constant change in weight was reached.

DETERMINATION OF ASH IN PRECIPITATED FRACTIONS

The sulfated ash of the precipitated fractions was determined by the analytical laboratory according to Institute Method 712 (1947). The ash was calculated as sodium chloride.

DETERMINATION OF THE OVENDRY FRACTION OF THE PRECIPITATED FRACTIONS

The ovendry fraction was determined according to Institute Method 3 (1951) by the analytical laboratory.

QUALITATIVE IDENTIFICATION OF SUGAR UNITS IN THE PRECIPITATED FRACTIONS

To determine the simple sugars in the unhydrolyzed fractions, about 90 mg. of the airdry sample were moistened with alcohol and then suspended in water for one hour with intermittent mixing. The suspension was filtered and portions of the filtrate were chromatographed separately in the acid and the pyridine systems.

To determine the simple sugars in the hydrolyzed fractions, about 90 mg. of the airdry sample was refluxed with 3 ml. of 0.5 N hydrochloric acid for three hours. Portions of the hydrolyzate were chromatographed separately in the acid and the pyridine systems.

QUANTITATIVE DETERMINATION OF SUGAR UNITS IN THE PRECIPITATED FRACTIONS

About 0.5 g. of the airdry sample was refluxed with 50 ml. of 3% sulfuric acid for 4 hours. After hydrolysis, about 40 mg. of accurately weighed ribose were added, and the hydrolyzates were neutralized to a pH of 6.0 with a saturated barium hydroxide solution. The barium sulfate was removed by filtering through a celite pad. The filtered solutions were passed through an Amberlite IR-120 cation exchange column and an Amberlite IR-4B(OAc^-) anion exchange column. The final pH was about 3.5. The deionized solutions were colorless. They were concentrated *in vacuo* at 22°C. to about 3 ml. The sugars were separated by chromatography and determined quantitatively.

QUALITATIVE AND QUANTITATIVE DETERMINATION OF SUGAR UNITS IN FRACTIONS ISOLATED AS SOLUTIONS

A portion of the solution was treated with 72% sulfuric acid to adjust the pH to about 0.5. The sample was refluxed 4 hours and then neutralized and concentrated as above. Qualitative chromatograms were made first. If sugars were present in significant amounts they were then determined quantitatively.

EVALUATION OF SEVERAL ANALYTICAL METHODS

QUANTITATIVE DETERMINATION OF SUGARS

The precision of the sodium periodate oxidation used in the quantitative determination of sugars was demonstrated by measuring the formic acid obtained in the oxidation of solutions of pure sugars. Data are given in Table II.

The accuracy of the method for the quantitative determination of sugars was demonstrated with a solution of glucose, arabinose and ribose. The amount of glucose and arabinose was measured using ribose as the reference sugar. Recovery data are given in Table III.

SOLUBLE LIGNIN DETERMINATION

The amount of lignin which remained dissolved in the acid filtrates from the Klason lignin determination was estimated from the ultraviolet absorbance of the filtrates. The determination is based on the expression in Equation (1).

$$\underline{C} = \underline{A}/ba \qquad (1)$$

where $\underline{C}$ = concentration of lignin in grams per liter

b = internal cell length in cm. (constant)

$\underline{A}$ = absorbance (measured)

a = absorptivity (constant)

There are many uncertainties in this determination. One serious source of error may be in the selection of a value for the absorptivity

TABLE II

PRECISION OBTAINED IN THE SODIUM PERIODATE OXIDATION OF PURE SUGARS

Glucose, mg.	Arabinose, mg.	Ribose, mg.	Galactose, mg.	Xylose, mg.
1.87	1.86	1.83	0.89	0.92
1.86	1.87	1.81	0.89	0.93
1.89	1.87	1.84	0.88	0.92
1.87	1.84	1.78	0.88	0.92
1.88	1.84	1.80	0.85	0.93
1.84	1.85	1.81	0.85	0.92
1.84	1.81		0.86	0.90
1.87			0.87	0.92
σ = 0.02	σ = 0.02	σ = 0.02	σ = 0.01	σ = 0.01

TABLE III

ACCURACY OF THE METHOD OF QUANTITATIVE DETERMINATION OF SUGARS

Arabinose, % Recovery	Glucose, % Recovery
101.0	100.5
100.0	101.0
97.6	98.0
100.5	101.5
101.0	98.0
100.5	99.0

of lignin. For this thesis, a value was taken from the data for the absorptivity of isolated aspen native lignin dissolved in dioxane which was determined by Buchanan, Brauns and Leaf (15). The relationship between the ultraviolet absorption of isolated native lignin and that of the remainder of the lignin is not known. Neither is it clearly known how the absorption is changed by pulping and bleaching treatments, although there is evidence which indicates that the ultraviolet absorption of isolated native lignin was not drastically changed by sulfonation (16), chlorination in water, or isolation with acids (17).

Another error may be caused by the carbohydrate dehydration products (furfural, hydroxymethylfurfural, and other intermediate products) formed in the 3% acid stage of the Klason lignin determination, which may contribute to the absorbance of the filtrates. The absorbance of the acid filtrates from the Klason lignin determination on the unbleached pulp used in this thesis and on simple sugars representative of the carbohydrate fraction of that pulp are illustrated by curves 1 and 2 in Figure 3.

As can be seen from curve 1, the contribution from the carbohydrate dehydration products was highest at 280 mmu and much lower at 230 mmu. The absorptivity of isolated native lignin was shown by Buchanan, Brauns and Leaf (15) to be much higher at 230 mmu, where it was 42, than at 280 mmu, where it was 15. Thus, the effect of the carbohydrate dehydration products would be minimized if the concentration of soluble lignin was estimated by Equation (1) at 230 mmu. However, the error would not be completely eliminated and therefore, the value for soluble lignin would be somewhat high.

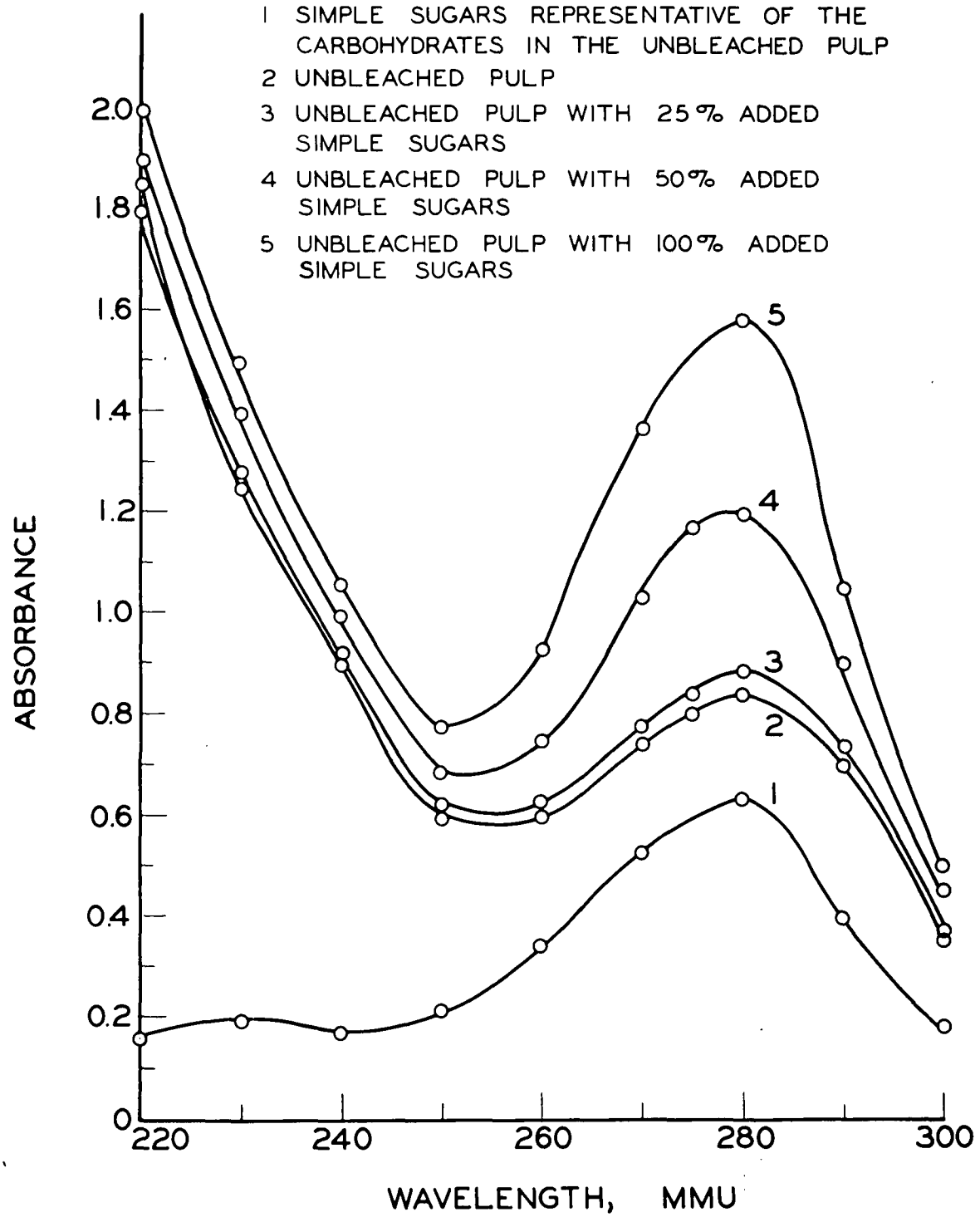

Figure 3. Absorbance of the Filtrates from the Klason Lignin Determination on Mixtures of Pulps and Simple Sugars

Browning and Bublitz (18) suggested correcting for the carbohydrate interference by calculating the soluble lignin concentration using simultaneous equations as for example Equations (2) and (3).

$$a_{c-230}\,\underline{C}_c + a_{l-230}\,\underline{C}_l = \underline{A}_{230} \qquad (2)$$

$$a_{c-280}\,\underline{C}_c + a_{l-280}\,\underline{C}_l = \underline{A}_{280} \qquad (3)$$

In these equations, a_{c-230} and a_{c-280} represent the absorptivities of the carbohydrates and their reaction products of concentration $\underline{C}_c$ at 230 and 280 mmu, respectively. The absorptivities for the carbohydrate materials were obtained by subjecting pure simple sugars, representative of the carbohydrate fraction of the pulp, to conditions obtained in the lignin determination.

However, the value for soluble lignin obtained from these expressions may be low. The insoluble lignin may condense with carbohydrate dehydration products (19) and remove them from solution. Then, the correction based on the absorbance of the dehydration products of pure sugars in the absence of lignin would be too high, and therefore, the value for soluble lignin low.

The ability of the insoluble lignin to remove carbohydrate dehydration products was studied in this thesis by measuring the increase in absorbance of the lignin filtrates, when the carbohydrate fraction of the unbleached pulp was increased by adding simple sugars prior to the lignin determination. The carbohydrate fraction was increased (A) 25%, (B) 50%, and (C) 100%. Two tests were made. In one the amount of acid was constant based on the amount of pulp present as prescribed by the

Klason lignin method (20 ml. acid per 1 gram of pulp). In the second test the amount of acid was adjusted to the total weight of pulp and carbohydrates. The results are given in Figure 3 and Table IV. Since the ultraviolet absorbance did not increase the expected amounts, it was indicated that carbohydrate dehydration products may have been removed by the insoluble lignin. As discussed above, this would cause the value for soluble lignin as determined from Equations (2) and (3) to be low.

It is very probable that the removal of carbohydrate dehydration products by the insoluble lignin is a function of the amount of the insoluble lignin present. Therefore, in the case of the unbleached pulps whose lignin content is high, the contribution of the carbohydrate products to the absorbance of the lignin filtrate may be very small. Then, the value for soluble lignin determined by Equation (1) at 230 mmu may be the best estimate. In the case of the chlorinated and the caustic-extracted pulps whose lignin content is low, the contribution of the carbohydrate products to the absorbance of the lignin filtrates may be very significant. Then, the best estimate for soluble lignin may be obtained using Equation(2) and (3). Since this point was not investigated further, both the value for soluble lignin estimated by Equation (1) and the simultaneous equations [Equations (2) and (3)] will be reported for comparative purposes.

Although it appears that the insoluble lignin removes carbohydrate dehydration products, the data in Table IV indicates that the weight of the material removed is insufficient to affect the yields of the insoluble (Klason) lignin. This can be explained by noting the high absorptivity

TABLE IV

EFFECT OF SIMPLE SUGARS ON THE ULTRAVIOLET ABSORBANCE OF LIGNIN FILTRATES FROM UNBLEACHED PULP

	Simple Sugars	Amount of Simple Sugars Per Cent of Carbohydrate Fraction of the Pulp			
		0	25	50	100
Test 1					
Vol. 72% H_2SO_4 (ml.)	20	20	20	20	20
Measured absorbance at 280 mmu	1.25	.910	.950	1.18	1.50
Calculated absorbance at 280 mmu	--	--	1.11	1.31	1.71
Per cent of expected increase in absorbance	--	--	20	68	74
Yield of Klason lignin	---	11.5	11.5	11.4	11.4
Test 2					
Vol. 72% H_2SO_4 (ml.)	20	20	25	--	40
Measured absorbance at 280 mmu	1.25	.710	.730	--	1.00
Calculated absorbance at 280 mmu	--	--	.85	--	1.25
Per cent of calculated increase in absorbance actually found	--	--	15	--	54

of carbohydrate dehydration products. For example, the absorptivity of furfural is 100 at 280 mmu as compared with 1.25 as found for the carbohydrate products from the pulp.

HOLOCELLULOSE DETERMINATION

A modification of the Wethern technique for isolating holocellulose was selected since the conditions of preparation were milder than other holocellulose methods. It was demonstrated that the yields of a holocellulose prepared in this manner are nearly identical with the yields of chlorite holocellulose and it was shown that only small amounts of carbohydrates were present in the holocellulose liquors indicating that essentially all of the carbohydrates were retained in the holocellulose residue. Less than 1% lignin, as determined by the Klason and soluble lignin methods, remained in the holocellulose.

The yields of holocellulose prepared by several variations of Wethern's procedure are compared in Table V with the yields obtained by the chlorite method for the three pulps studied in this work. It was found that for pulps, the number and duration of chlorinations could be reduced without affecting the yield. Furthermore, the yields of holocellulose prepared by the modified Wethern technique are similar to those obtained by the chlorite procedure for the unbleached and chlorinated pulps. In the case of caustic-extracted pulps, the chlorite procedure gave higher yields. However, there is good evidence that the chlorite holocellulose contained significant amounts of lignin. They gave very positive Maule tests and the yield was reduced by an additional treatment. Also, the higher yields given by the chlorite method

TABLE V

YIELDS FROM VARIOUS HOLOCELLULOSE PREPARATIONS

	Yield of Holocellulose Based on Pulp Analyzed, %	Yield of Holocellulose Unbleached Pulp Basis, %
UNBLEACHED PULP		
Wethern Procedure		
5 chlorinations (7 min. each)	83.7	83.7
4 chlorinations (7 min. each)	84.1	84.1
3 chlorinations (5,3,3 min.)	84.2	84.2
Chlorite Procedure		
2 treatments (1 hour each)	83.6	83.6
CHLORINATED PULP		
Wethern Procedure		
3 chlorinations (5,3,3 min.)	91.0	81.8
Chlorite Procedure		
1 treatment (0.5 hour)	90.9	81.7
CAUSTIC-EXTRACTED PULP		
Wethern Procedure		
3 chlorinations (5,3,3 min.)	94.1	80.9
Chlorite Procedure		
2 treatments (1 hour each)	95.5	82.1
1 treatment (0.5 hour)	96.1	82.6

would indicate an increase in the absolute amount of holocellulose during the caustic-extraction stage, whereas the values from the Wethern technique would indicate a decrease.

The Klason lignin content of the holocellulose from the unbleached pulp prepared by using three chlorinations was 0.3% and the soluble lignin content was 0.6%.

The spent liquors from the preparation of holocellulose from an unbleached pulp were analyzed for carbohydrates. The scheme of analysis is shown in Figure 4.

When all of the extraction liquors were combined, a cream-colored, flocculent precipitate formed (Fraction 1). This contained carbohydrates. The entire fraction, however, was less than 1% of the pulp.

A sample of the supernatant solution was acidified with acetic acid, concentrated *in vacuo*, and then passed through an Amberlite IR-120 cation exchange column to remove ethanolamine. Some material precipitated on the column, and this was washed off with alcohol. No sugars were indicated by chromatograms of the unhydrolyzed or hydrolyzed fraction (Fraction 2). The material retained by the column was eluted with 1 *N* sulfuric acid. No sugars were indicated by chromatograms of the unhydrolyzed, eluted material (Fraction 3).

The effluent from the cation column was repeatedly concentrated *in vacuo* and diluted with alcohol. A large amount of a crystalline precipitate formed (Fraction 4) which was probably a salt of ethanolamine. Fraction 4 gave a negative Molisch test. The concentrated solution

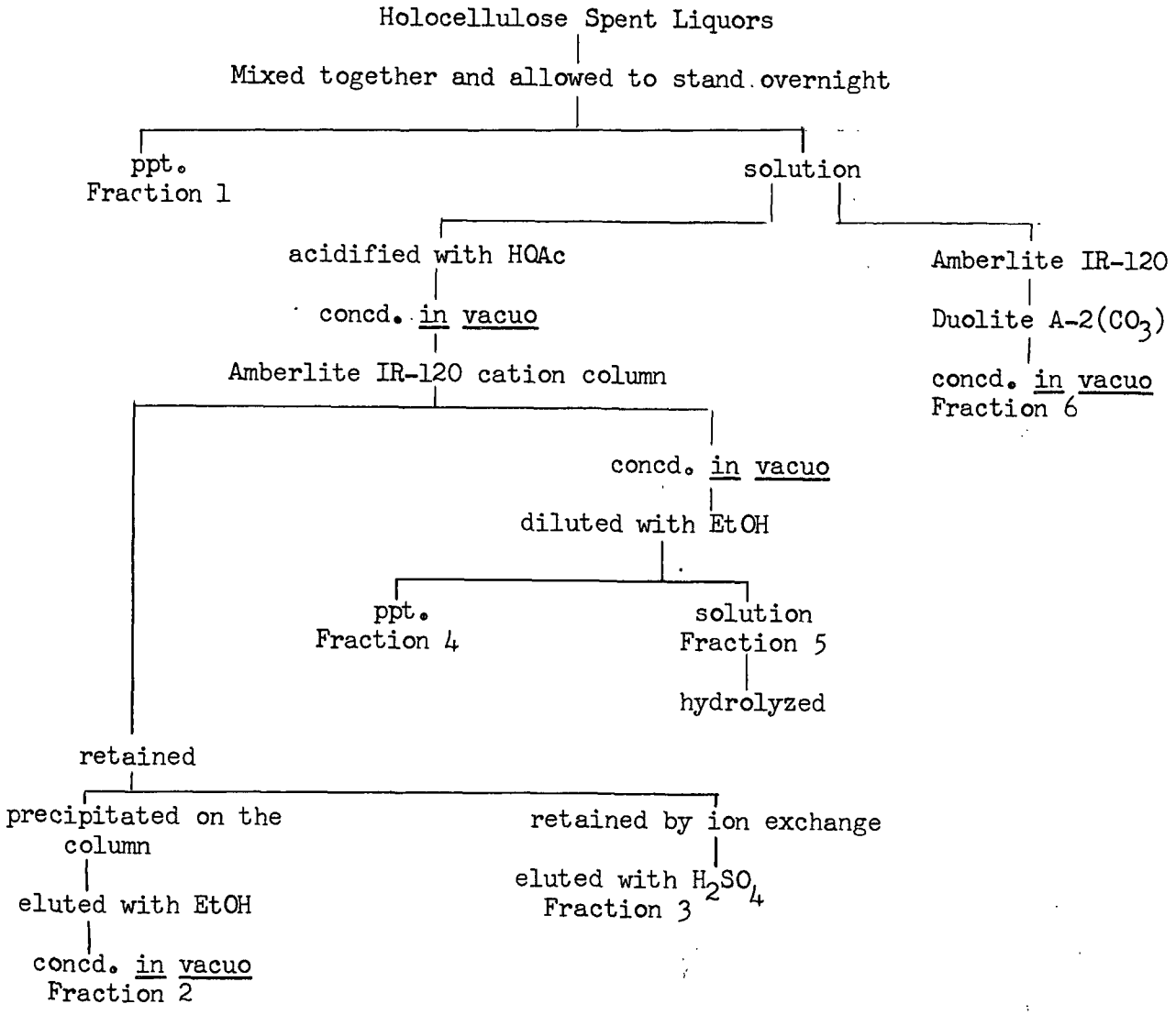

Figure 4. Fractionation of Holocellulose Spent Liquor

(Fraction 5) was hydrolyzed. A chromatogram of the hydrolyzed solution did not indicate carbohydrates. However, when xylose was mixed with Fraction 5 and the mixture chromatographed (unhydrolyzed), six sugar spots were indicated. Since the solution was strongly acid it is possible that the xylose reverted to oligosaccharides of some type. After treating Fraction 5 with an anion resin or with charcoal, it no longer affected xylose.

If carbohydrates originating in the pulp had been in Fraction 5, the component that attacked the xylose could have degraded them beyond the state of simple sugars. In that case, they would not have been found by this scheme of analysis. Therefore, it was attempted to remove this component as soon as possible and while the solution was still dilute. A fresh portion of the supernatant spent liquor was immediately passed through an Amberlite IR-120 cation column and a Duolite A-2(CO_3) anion column. The deionized solution (Fraction 6) was then concentrated in vacuo. Paper chromatograms indicated that no carbohydrates were present in either the unhydrolyzed or the hydrolyzed solution.

It was qualitatively demonstrated in a repeated run through the deionization procedure that if carbohydrates had been present in the supernatant liquor, they would have persisted through the scheme of analysis. Mannose (1% on the pulp basis) was added to the liquor before deionization and it was qualitatively identified in the deionized liquor by paper chromatography.

Summarizing these results, the only carbohydrates found in the spent liquors from a holocellulose determination on the unbleached pulp were

in Fraction 1. This same fraction was also isolated in the spent liquors from a holocellulose determination of the chlorinated and caustic-extracted pulps. The total fraction was 0.80% of the unbleached pulp, 0.40% of the chlorinated pulp, and 0.25% of the caustic-extracted pulp. After hydrolysis, chromatograms indicated the presence of arabinose and traces of galactose and xylose. By comparing the intensity of these spots on the chromatogram with spots containing known amounts of sugar, it was estimated that the carbohydrate part of these fractions was less than 50%.

EXPERIMENTAL RESULTS

PREPARATION OF UNBLEACHED AND PARTIALLY BLEACHED PULPS

EXPERIMENTAL DATA FROM THE PREPARATION OF UNBLEACHED PULP

The cooking conditions and yield data for the unbleached pulps are given in Table VI.

TABLE VI

PULPING DATA

Cook number	1	2	3	4
Chemical (ovendry wood basis)				
Sodium sulfite as Na_2SO_3, %	12	12	12	12
Sodium carbonate as Na_2CO_3, %	5.75	5.75	5.75	5.75
Water ratio	4	4	4	4
Maximum temperature, °C.	170	170	170	170
Time to max. temp., min.	120	120	120	120
Time at max. temp., min.	90	90	90	90
Maximum pressure, p.s.i.	116	120	120	118
Relief time, min.	15	15	15	15
pH of cooking liquor	11.30	11.30	11.30	11.30
pH of spent liquor	9.30	9.30	9.35	9.35
Chip charge, ovendry, g.	3578	3578	3578	3578
Pulp yield, ovendry, g.	2726	2731	2715	2721
Pulp yield, %	76.2	76.3	75.9	76.1
Holocellulose content, % [1]	86.1	86.1	85.9	85.8

[1] Average of duplicate determinations expressed on the ovendry pulp basis.

EXPERIMENTAL DATA ON THE LOSS OF CARBOHYDRATE MATERIAL IN THE PRETREATMENT OF UNBLEACHED PULPS

The liquors from the pretreatment soaking stage (see page 13) were acidified with acetic acid and concentrated *in vacuo*. Two volumes of alcohol were added and a white flocculent precipitate formed, which was separated by centrifuging, and then washed twice with hot alcohol, twice with ether, twice with petroleum ether and air dried.

A chromatogram of the hydrolyzed precipitate indicated predominantly xylose with small amounts of arabinose, galactose and glucose. A brick-red colored spot appeared slightly below mannose on the chromatogram developed in the acid system but was held at the starting line on the chromatogram developed in the pyridine system. This probably was an aldobiuronic acid (20).

The yield and composition of the precipitate is given in Table VII.

TABLE VII

YIELD OF ALCOHOL-INSOLUBLE MATERIAL REMOVED IN THE PRETREATMENT STAGE

	1	2
Weight pulp (ovendry, g.)	187.0	187.0
Total volume water, ml.	3400	3400
Final pH of water	8.1	8.3
Weight of precipitate (ovendry, g.)	0.35	0.38
Yield of precipitate, % ovendry pulp	0.19	0.21

A chromatogram of the supernatant alcohol solution from the precipitation step did not indicate the presence of sugars.

EXPERIMENTAL DATA FROM THE PREPARATION OF CHLORINATED CAUSTIC-EXTRACTED AND HYPOCHLORITE-TREATED PULPS

The experimental conditions and data for the chlorination-and caustic-extraction stages are given in Tables VIII and IX, respectively. The brightness values of the pulps finally bleached with calcium hypochlorite are given in Table X.

ANALYSIS OF PULP RESIDUES

The preparation of pulp residues for analysis is presented schematically in Figure 5. Two samples of the air-dried composite unbleached pulp were presoaked with distilled water, then separately chlorinated and the yields determined. The moist chlorinated pulp samples were combined, mixed and then duplicate samples were caustic extracted. The caustic-extracted pulps were combined for analysis after determining their yields.

The scheme of analysis of the pulp residues is shown in Figure 6. A portion of the moist composite pulp was air dried for the determination of lignin, pentosans, uronic acid and ash. Duplicate holocellulose determinations were made on the moist composite pulp. After determining yields, the holocellulose samples were combined, thoroughly mixed and then duplicate alkali-resistant cellulose and hemicellulose determinations were made. These were each combined and hydrolyzed and the simple sugar composition of the hydrolyzates was determined.

The results of the analysis of the unbleached pulp, chlorinated pulp and caustic-extracted pulp are given in Tables XI, XII, and XIII, respectively.

TABLE VIII

CONDITIONS OF CHLORINATION AND YIELD DATA

Chlorination	2	3	4	5	6	7
Pulp sample	NSSC-2[1]	NSSC-3[2]	NSSC-3	NSSC-3	NSSC-3	NSSC-3
Conditions of chlorination						
a. Consistency, %	3.0	2.5	3.0	3.0	3.0	3.0
g. ovendry pulp	90.4	406.7	300.6	414.8	409.8	408.9
ml. water	2913	15873	9720	13476	13250	13221
b. Chlorine (% ovendry pulp basis)	12	12	12	12	12	12
strength of chlorine water (g./l.)	4.52	6.20	5.71	6.00	6.28	6.05
ml. chlorine water	2400	7860	6320	8320	7840	8150
c. Temperature, °C.	25	20	20	20	20	20
d. Time, min.	30	60	70	70	73	71
Yield						
a. g. ovendry chlorinated pulp	81.4	357.5	269.1	366.7	369.6	369.8
b. Yield, % unbleached pulp	89.9	87.9	89.5	88.4	90.5	90.8
Disposition of pulp	discarded	discarded	discarded	caustic extraction 5	pulp analysis & caustic extraction 6 and 7	
Disposition of liquor	preliminary liquor analysis	preliminary liquor analysis	quantitative liquor analysis	discarded	discarded	

[1] Pulp NSSC-2 Pulp No. 4 by D. C. Lea (24)

[2] Pulp NSSC-3 - See pages 11 and 37.

TABLE IX

CONDITIONS OF CAUSTIC EXTRACTION AND YIELD DATA

Caustic extraction	4	5	6	7
Pulp from chlorination	3	5	6 & 7	6 & 7
Conditions of caustic extraction				
a. Consistency, %	10	8.2	8.2	8.2
g. ovendry pulp	77.5	359.4	191.3	191.9
ml. water	699		1774	1778
b. NaOH (% ovendry pulp basis)	2	2	2	2
c. Temperature, °C.	50	50	50	50
d. Time, min.	60	60	60	60
Yield				
a. g. ovendry caustic-extracted pulp	72.3	345.3	181.0	182.4
b. yield, % chlorinated pulp	93.4	96.1	94.6	95.0
c. yield, % unbleached pulp	82.1	85.1	85.7	86.0
Disposition of pulp	discarded	discarded	quantitative pulp analysis	
Disposition of liquor	preliminary liquor analysis	quantitative liquor analysis	discarded	

TABLE X

FINAL BRIGHTNESS ATTAINED
AFTER HYPOCHLORITE STAGE

Active Chlorine, % of Ovendry Pulp	Brightness
0.5[1]	58.0
1.5[1]	67.4
3.0[1]	75.6
4.0[2]	81.0
6.0[2]	83.0

[1] Active chlorine was completely consumed.

[2] Active chlorine was not completely consumed. The reaction went for three hours.

TABLE XI

ANALYTICAL DATA FOR THE UNBLEACHED PULP
(Composite Pulp from Cooks 1, 2, 3 & 4)

	A	B	Av.
Ash[1]			
Sulfated ash, %	1.40	1.38	1.39
Ash as Ca and Na, %	0.43	0.43	0.43
Lignin and extractives[2]			
95% alcohol soluble, %	1.20	1.26	1.2
Klason lignin, %	9.92	10.13	10.0
Soluble lignin			
a. Calculated by equation (1), 230 mmu, %	4.69	4.42	4.6
b. Calculated by equations (2) and (3), %	3.62	3.25	3.5
Carbohydrates			
Holocellulose, %[3]	85.31	84.95	85.2
a. Sulfated ash, %[4]	0.61	0.58	0.60
b. Ash as Ca and Na, %[4]	0.20	0.19	0.20
c. Nitrogen, %[4]	0.29	0.30	0.30
Alkali-resistant cellulose[4]	74.33	74.37	74.4
a. Sulfated ash, %[5]	0.26[7]	0.29[7]	---
b. Ash as K, %[5]	0.12[7]	0.13[7]	---
Hemicelluloses, %[4]	24.10	24.11	24.1
a. Sulfated ash, %[6]	8.82[7]	8.60[7]	---
b. Ash as K, %[6]	3.96[7]	3.86[7]	---
Pentosans[2]			
a. Uncorrected for uronic acids, %	19.07	18.88	19.0
b. Corrected for uronic acids, %	18.03	17.84	17.9
Uronic acids[2]			
a. As CO_2, %	0.97	0.97	0.97
b. As uronic anhydride, %	3.88	3.88	3.88

1 Ovendry, unbleached pulp basis
2 Ovendry, ash-free, unbleached pulp basis
3 Ovendry, ash-free, unbleached pulp basis (product also corrected for ash)
4 Ovendry, composite holocellulose basis
5 Ovendry, alkali-resistant cellulose basis
6 Ovendry, hemicellulose basis
7 Average of duplicate determinations on sample A and B, respectively.

TABLE XII

ANALYTICAL DATA FOR CHLORINATED PULP
(Composite Chlorinated Pulp 6 & 7)

	A	B	Av.
Ash[1]			
Sulfated ash, %	0.21	0.28	0.25
Ash as Ca and Na, %	0.06	0.09	0.08
Lignin and extractives [2]			
95% alcohol soluble, %	6.05	5.76	5.9
Klason lignin, %	2.73	2.74	2.7
Soluble lignin			
a. Calculated by equation (1), 230 mmu, %	2.29	2.19	2.2
b. Calculated by equation (2) and (3), %	0.77	0.59	0.7
Carbohydrates			
Holocellulose, % [3]	93.14	93.17	93.2
a. Sulfated ash, % [4]	0.45	0.33	0.39
b. Ash as Ca and Na, % [4]	0.15	0.11	0.13
c. Nitrogen, % [4]	0.22	0.23	0.23
Alkali-resistant cellulose, % [4]	75.40[7]	75.14[7]	75.2
a. Sulfated ash, % [5]	0.38[7]	0.40[7]	--
b. Ash as K, % [5]	0.17[7]	0.18[7]	--
Hemicelluloses, % [4]	24.16[7]	24.14[7]	24.2
a. Sulfated ash, % [6]	8.35[7]	9.62[7]	--
b. Ash as K, % [6]	3.74[7]	4.31[7]	--
Pentosans [2]			
a. Uncorrected for uronic acids, %	21.17	20.87	21.0
b. Corrected for uronic acids, %	20.08	19.78	19.9
Uronic acids [2]			
a. As CO_2, %	1.00	1.04	1.02
b. As uronic anhydride, %	4.00	4.16	4.08

[1] Ovendry, chlorinated pulp basis
[2] Ovendry ash-free, chlorinated pulp basis
[3] Ovendry, ash-free, chlorinated pulp basis (product also corrected for ash)
[4] Ovendry, composite holocellulose basis
[5] Ovendry, alkali-resistant cellulose basis
[6] Ovendry, hemicellulose basis .
[7] Average of duplicate determinations on samples A and B, respectively.

TABLE XIII

ANALYTICAL DATA FOR CAUSTIC-EXTRACTED PULPS
(Composite Caustic Extracted Pulp 6 & 7)

	A	B	Av.
Ash [1]			
Sulfated ash, %	0.72	0.99	0.85
Ash as Na, %	0.24	0.32	0.28
Lignin and extractives [2]			
95% alcohol soluble, %	0.76	0.88	0.8
Klason lignin, %	2.42	2.35	2.4
Soluble lignin			
a. Calculated by equation (1) 230 mmu, %	1.92	1.86	1.9
b. Calculated by equations (2) and (3), %	0.37	0.33	0.3
Carbohydrates			
Holocellulose, % [3]	97.10	97.27	97.2
a. Sulfated ash, % [4]	0.45	0.40	0.43
b. Ash as Na, % [4]	0.15	0.15	0.14
c. Nitrogen, % [4]	0.20	0.20	0.20
Alkali-resistant cellulose, % [4]	75.48[7]	75.82[7]	75.7
a. Sulfated ash, % [5]	0.42[7]	0.52[7]	--
b. Ash as K, % [5]	0.19[7]	0.23[7]	--
Hemicelluloses, % [4]	23.69[7]	23.59[7]	23.6
a. Sulfated ash, % [6]	7.56[7]	9.24[7]	--
b. Ash as K, % [6]	3.39[7]	4.14[7]	--
Pentosans [2]			
a. Uncorrected for uronic acids, %	21.85	21.61	21.7
b. Corrected for uronic acids, %	20.75	20.51	20.6
Uronic acids [2]			
a. As CO_2, %	1.05	1.02	1.03
b. As uronic anhydride, %	4.20	4.08	4.14

[1] Ovendry, caustic-extracted pulp basis
[2] Ovendry, ash-free caustic-extracted pulp basis
[3] Ovendry, ash-free, caustic-extracted pulp basis (product also corrected for ash)
[4] Ovendry, composite holocellulose basis
[5] Ovendry, alkali-resistant cellulose basis
[6] Ovendry, hemicellulose basis
[7] Average of duplicate determinations on samples A and B, respectively.

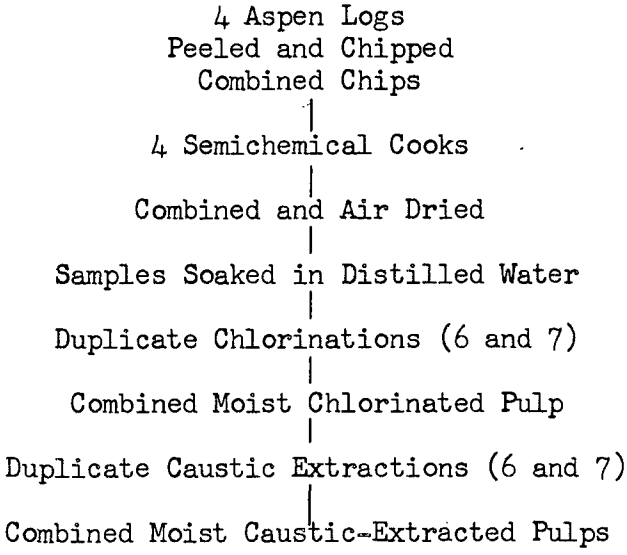

Figure 5. Scheme of Preparation of Pulp Residues for Analysis

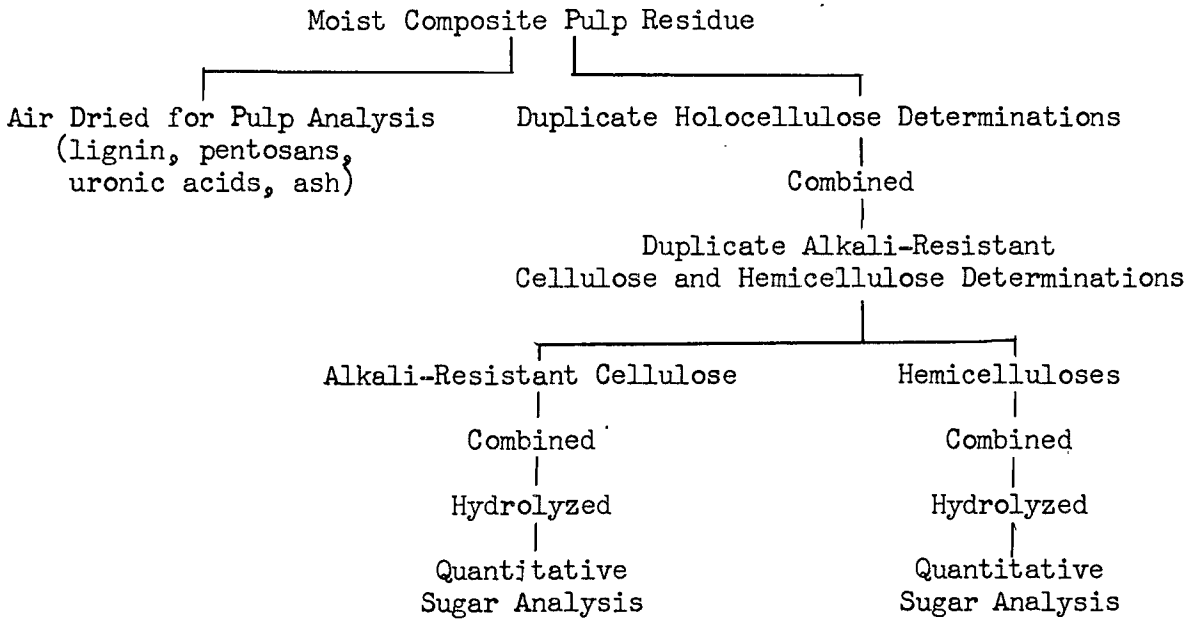

Figure 6. Scheme of Analysis of Pulp Residues

The data from the analysis of simple sugars in the hydrolyzates of the alkali-resistant celluloses are given in Table XIV. The amount of a simple sugar is expressed as the percentage of the total simple sugars found in the hydrolyzate. Apparently there was either material in the hydrolyzate or impurities in the chromatographic solution which collected at the bottom of the chromatogram near the ribose which caused the blank in that region to be several times higher than that found on other areas of the chromatogram. This made the correction for the ribose titration uncertain. Therefore, ribose was not used as a reference sugar to calculate the sugar components on the basis of the alkali-resistant cellulose but rather, the sugars were calculated as a ratio of total sugars found in the hydrolyzate.

The data from the analysis of simple sugars in the hydrolyzates of the hemicelluloses are given in Table XV. The results are expressed as the percentage polysaccharide on the ovendry, ash-free hemicellulose basis. Considerable amounts of uronic acid material were indicated as well as traces of glucose and mannose.

FRACTIONATION OF THE LIQUORS FROM THE CHLORINATION STAGE

PRELIMINARY EXPERIMENTS AND OBSERVATIONS

It was first attempted to separate the lignin and carbohydrate material using ion exchange columns. A sample of chlorination liquor 2 was passed through an Ionac C-200 cation exchange column and a Duolite A-2 (OH) anion exchange column. After hydrolysis of the de-ionized liquor, only insignificant amounts of sugars were found

TABLE XIV

RATIO OF SIMPLE SUGARS PRESENT IN THE HYDROLYZATES FROM ALKALI-RESISTANT CELLULOSE

	Alkali-Resistant Cellulose from Unbleached Pulp[2]			Alkali-Resistant Cellulose from Chlorinated Pulp[2]		
	Glucose, %	Mannose, %	Xylose, %	Glucose, %	Mannose, %	Xylose, %
	95.6	1.0	3.4	95.9	1.2	2.9
	95.4	1.5	3.1	96.5	1.0	2.5
	96.5	1.1	2.4	97.0	1.0	2.0
	97.0	1.1	1.9	96.3	1.2	2.5
	96.4	1.2	2.4	Av. 96.4	1.1	2.5
	96.6	1.0	2.4			
	96.2	1.3	2.5			
Av.	96.2	1.2	2.6			

	Alkali-Resistant Cellulose from Caustic-Extracted Pulp[2]		
	Glucose, %	Mannose, %	Xylose, %
	96.8	1.2	2.0
	96.5	1.3	2.2
	97.0	0.7	2.3
	96.6	1.6	1.8
	96.4	1.3	2.3
Av.	96.6	1.2	2.1

[1] Expressed as the percentage of the total simple sugars found after hydrolysis.

[2] Traces of galactose also present.

TABLE XV

SIMPLE SUGAR COMPOSITION OF THE HYDROLYZATES FROM THE HEMICELLULOSES[1]

Hemicellulose from Unbleached Pulp			Hemicellulose from Chlorinated Pulp		
Galactan, %	Araban, %	Xylan, %	Galactan, %	Araban, %	Xylan, %
--	--	78.6	0.5	0.5	--
0.8	0.8	--	1.1	0.4	--
0.9	0.8	--	0.5	--	77.2
--	--	78.5	--	--	78.3
--	--	78.2	0.4	0.4	76.3
1.4	0.8	--	0.5	0.5	--
1.0	1.1	--	--	--	79.0
Av. 1.0	0.9	78.5	--	--	81.2
			Av. 0.6	0.5	78.4

Hemicelluloses from Caustic-Extracted Pulp		
Galactan, %	Araban, %	Xylan, %
--	0.4	--
--	--	78.4
0.6	0.4	--
--	--	79.4
--	--	75.1
--	--	78.9
0.3	--	--
0.3	--	77.3
0.4	0.5	77.3
--	--	82.2
Av. 0.4	0.4	78.3

[1] Polysaccharide expressed as percentage of ovendry ash-free hemicellulose.

(Table XVI). The total weight of the sugars was only 0.2% of the material removed in chlorination or about 0.02% of the unbleached pulp.

TABLE XVI

AMOUNTS OF SUGARS PRESENT AFTER HYDROLYSIS OF CHLORINATION LIQUOR 2

Basis--90.4 g. Ovendry Unbleached Pulp

Sugar	Weight, g.
Xylose	0.01
Glucose	0.008
Galactose	0.002
Arabinose	0.01

It was suspected that sugars might have been retained or destroyed by the ion exchange resins. Several resins were studied in respect to their retention of xylose from a solution of that sugar. The amount of sugar in the effluent was determined according to the method of Somogyi (21). The data are given in Table XVII.

TABLE XVII

RETENTION OF SUGARS BY ION EXCHANGE RESINS

Resin	Conc. of Xylose, g./l.	Vol. of Xylose Solution Used, ml.	Amt. of Wash Water, ml.	Retention, %
Amberlite IR-120 cation[1]	0.6	500	2000	0
Ionac C-200 cation[2]	0.6	500	2000	0
Amberlite IR-4B(OH) anion[1]	0.6	500	2500	20
Duolite A-2 (OH) anion[3]	0.6	500	2000	10
Amberlite IR-4B(CO_3) anion[1]	0.3	1000	3000	9.5
Duolite A-2 (CO_3) anion[3]	0.3	1000	2000	9

[1] Rohm and Haas Co., Philadelphia, Pa.

[2] The American Cyanamid Co., 30 Rockefeller Plaza, New York 20, N. Y.

[3] The Chemical Process Co., 58 Sutter St., San Francisco, Calif.

The retention of neutral carbohydrates by the ion exchange columns was not found to be sufficient to cause drastic errors in the determination of carbohydrates in the liquor. However, it is possible that a portion of the carbohydrates present was linked with acidic groups such as uronic acids, other acids resulting from carbohydrate oxidation or acidic lignin material. It is also possible that material precipitated on the columns as a result of the change in pH.

Because of these uncertainties a fractionation based on solubilities was then developed. First, an attempt was made to precipitate the lignin compounds from a sample of chlorination liquor 2 with basic lead acetate and with calcium hydroxide. It was possible to remove all color

with these two reagents and to reduce the ultraviolet absorptivities by 90%. However, it was found that these precipitating agents were not specific for lignin because material containing carbohydrates also precipitated from the chlorination liquor on the addition of a salt.

The precipitation of a considerable amount of material on addition of a salt indicated that much of the material removed in chlorination was in a colloidal or suspended state. The following observations were made concerning the nature of this material present in the liquor:

1. The suspended material was not removed completely by centrifuging or supercentrifuging.
2. The suspended material was not removed entirely by filtering. It clogged a hard filter paper. Use of an asbestos bed or filter-aid failed to clear the liquor.
3. The suspended material could be coagulated by adding a salt.
4. The suspended material could be coagulated by adding a large amount of hydrochloric acid.
5. The suspended material did not appear fibrous under a microscope.

It was found that the amount of suspended material was related to the degree of agitation during chlorination. Two 100-g. samples of unbleached pulp were soaked overnight in 800 ml. distilled water. One sample was filtered by suction. The filtrate was then filtered through a double layer of Cenco" No. 13260 filter paper. The other sample was diluted with 2200 ml. distilled water and stirred with a small Lightnin' mixer (model V) for one hour and then filtered as above. The solids content of the two filtrates was 0.4 and 1.2% of the pulp, respectively. The material in suspension after the stirring action

formed a flocculent precipitate when sodium sulfate was added or when poured into alcohol. The precipitate gave a positive Molisch test and a faint Maule Test. Two 100-g. samples were chlorinated for 1 hour. One was gently agitated by swirling the bottle and the other was agitated with the Lightnin' mixer. The chlorination liquor and all washings from the first chlorination were almost clear. The chlorination liquor from the second chlorination was almost clear but the washings appeared very cloudy. The pulp from the second chlorination was very mushy in contrast to the pulp from the first chlorination. The pulp from the first chlorination was suspended in water and stirred 10 minutes with the small Lightnin' mixer. The water was then definitely cloudy.

On the basis of these observations it appears that material was removed during the chlorination stage as a result of the combined action of water and agitation as well as by the action of chlorine.

DEVELOPMENT OF THE SCHEME OF FRACTIONATION

The scheme of fractionation finally developed for the spent chlorination liquors in the preliminary work is illustrated in Figures 7 and 8. Data related to this preliminary fractionation are given in Table XVIII. The liquor used in this fractionation came from chlorination 3. The total liquor and washings were analyzed in two parts (liquor A and liquor B) because it was first thought that essentially all of the material removed by chlorination would have been in liquor A which included the initial chlorination liquor plus the first two washings. However, after the work was well in progress, it became apparent that there was considerable material yet in the remainder of the washings (liquor B).

TABLE XVIII

YIELDS AND QUALITATIVE TESTS OF THE LIQUOR FRACTIONS FROM CHLORINATION 3

Fraction	Per Cent of Pulp Yield Loss[1]	Maule Test	Molisch Test	Simple Sugars after Hydrolysis
A-1	11.5	pos.	pos.	Galactose Arabinose Xylose
A-2	8.5	pos.	--	Trace of Arabinose
A-3	1.6	pos.	neg.	
A-4	1.4	pos.	neg.	
A-5	--	--	--	
A-6	--	--	pos.	Galactose Arabinose Xylose
B-1	2.2	slight	pos.	
B-2	0.9	pos.	pos.	
B-3	24.0	pos.	slight	
B-4	--	--	--	

[1] Based on airdry weight of fractions uncorrected for ash.

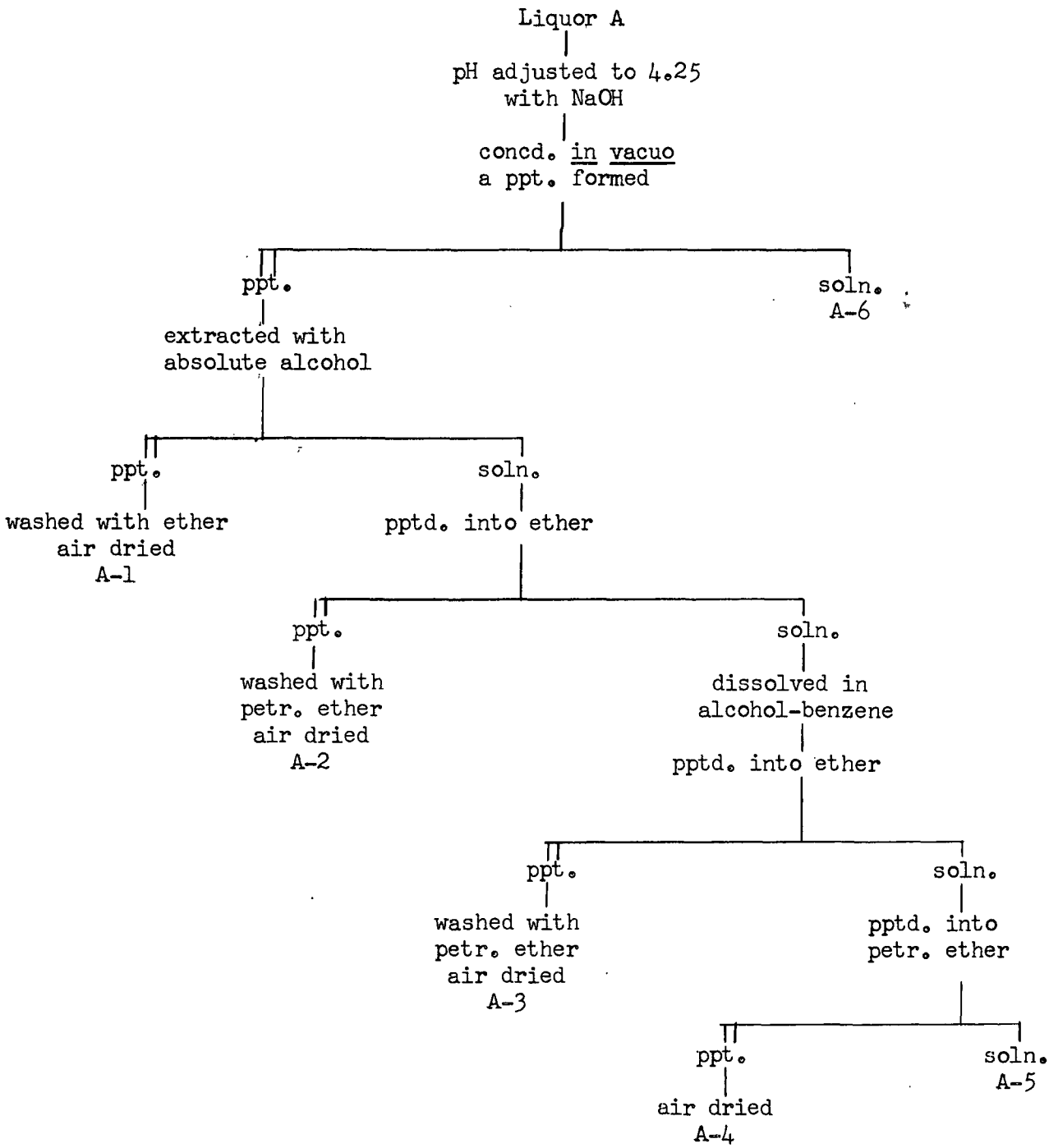

Figure 7. Scheme of Analysis of Liquor A from Chlorination 3

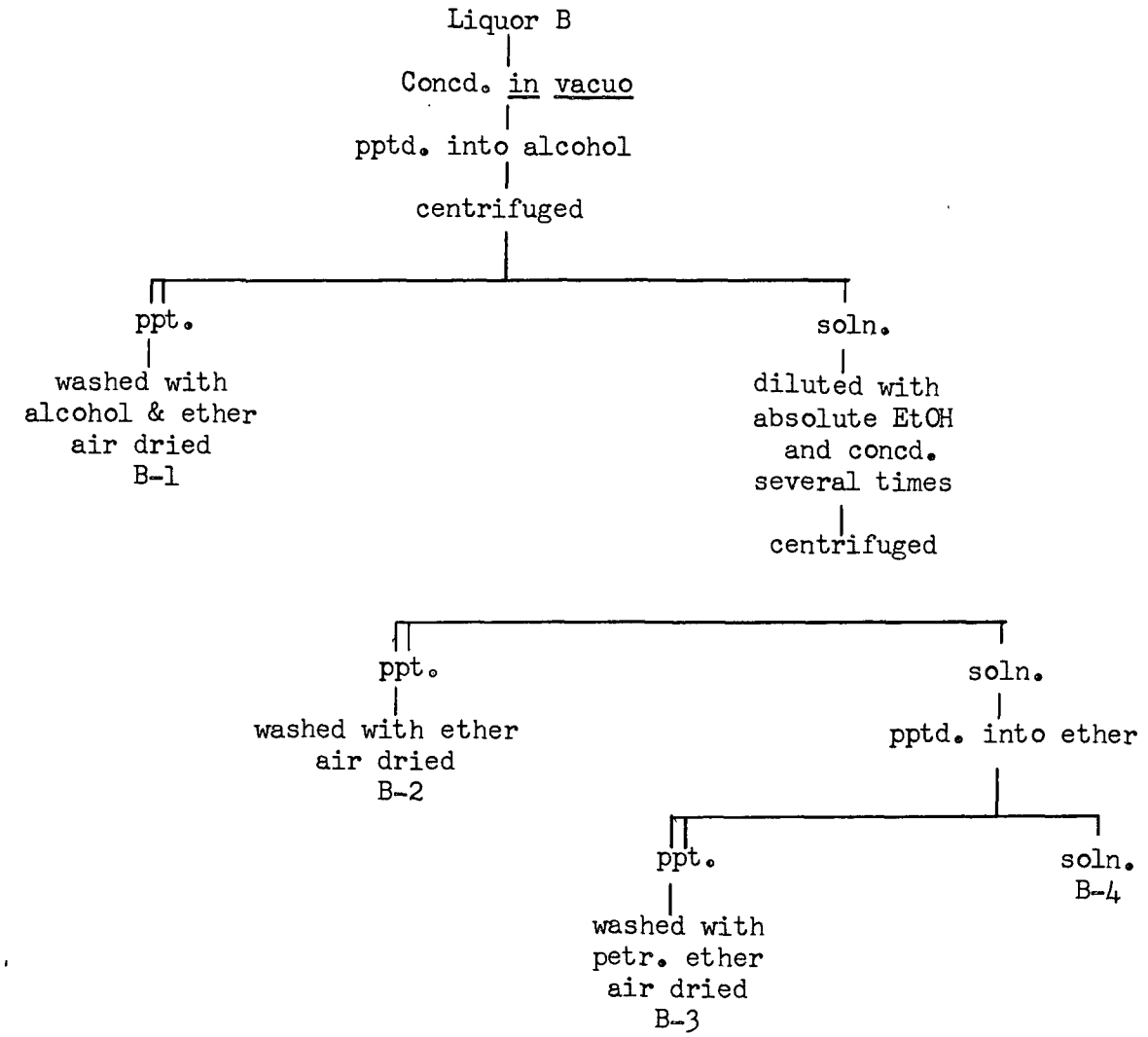

Figure 8. Scheme of Analysis of Liquor B from Chlorination 3

The first separation of liquor A (see Figure 7) resulted from adjusting the pH from 1.4 to 4.5 with sodium hydroxide and then concentrating *in vacuo*. Probably this material was salted out as the sodium chloride concentration increased. This precipitate was extracted by repeatedly suspending the fraction in absolute alcohol and then concentrating *in vacuo* in an attempt to dissolve the lignin and leave a carbohydrate residue. Although much material which showed a positive Maule test dissolved in the alcohol, the residue still contained material which gave a Maule test and contained 2.9% methoxyl on the airdry weight basis uncorrected for ash. It also contained carbohydrates as shown by the Molisch test and by a chromatogram of the hydrolyzate.

The alcohol-insoluble residue was insoluble in dioxane before hydrolysis. A dark-brown precipitate formed during hydrolysis and this precipitate was completely soluble in dioxane. Attempts were made to purify the carbohydrate portion by repeatedly (3 times) dissolving the precipitate in dilute potassium hydroxide solution, acidifying with acetic acid and precipitating with alcohol. However, the residue still gave a positive Maule test.

The presence of both lignin and carbohydrates in Fraction A-1 could have resulted from several different circumstances. They could have been simply a mixture resulting from coprecipitation. Acidic lignin products could have possibly been present as sodium salts which precipitated with the carbohydrates and as such would have resisted extraction by organic solvents. They could have been physically combined

if it is possible that small bits of fibers could have been dispersed in the chlorination. Also, the lignin and carbohydrates could have been chemically linked.

The alcohol-soluble material contained appreciable amounts of material giving a positive Maüle test. Much of this precipitated in ether (A-2) and (A-3), and smaller amounts, soluble in ether, were precipitated into low boiling petroleum ether (A-4). This later fraction was probably degraded lignin products of smaller molecular size and extractive material. There was also material soluble in the petroleum ether which probably was also extractive material and highly degraded lignin products.

A chromatogram of the hydrolyzed water-soluble fraction (A-6) indicated the presence of carbohydrates (galactose, arabinose and xylose). No further fractionation of this solution was made in this preliminary study.

Liquor B which consisted of all the washings (excepting the first two) was fractionated in the same way as liquor A except that the concentrated solution was treated directly with alcohol without going through the salting-out stage. It was surprising to find about three times as much material in fraction B-3 as that in A-2, an analogous fraction obtained from liquor A. It was thought that most of the material removed by chlorination would be present in the original liquor and the first two washings. This can perhaps be explained by the increase in pH (approaching pH 7) of the wash waters as the washing progressed.

QUANTITATIVE FRACTIONATION

To obtain quantitative data on the components of the chlorination liquor, the liquor and washings from chlorination 4 were fractionated according to the scheme shown in Figure 9, which, in general, is the scheme developed in the preliminary work. The combined liquor and wash water (initially at pH 1.3) was immediately treated with 1 N sodium hydroxide until a pH of about 4.0 was reached. The solution was filtered by gravity through a double layer of Cenco No. 13260 filter paper and was concentrated *in vacuo* at 35-45°C. from a volume of 40 liters to 160 ml. The precipitate which forms on concentrating was separated by centrifuging. The supernatant liquor did not deflect a light beam.

This precipitate was repeatedly suspended in absolute ethyl alcohol and concentrated *in vacuo*. The insoluble residue was washed with hot absolute alcohol until the washings were colorless, then twice with ether, twice with low boiling petroleum ether and was finally air dried (Fraction $Cl_2$4-1). Concentration of the alcohol washings yielded a second insoluble fraction (Fraction $Cl_2$4-2). The combined alcohol solutions (i.e., mother liquors from the two alcohol-insoluble fractions) were precipitated into ether according to the method described by Brauns (22) (Fraction $Cl_2$4-3). The ether solution was concentrated below room temperature by passing a stream of air across its surface and then dissolved in an alcohol-benzene solution and precipitated into low boiling petroleum ether (Fraction $Cl_2$4-5). The solids content of the petroleum ether solution was determined (Fraction $Cl_2$4-S-4).

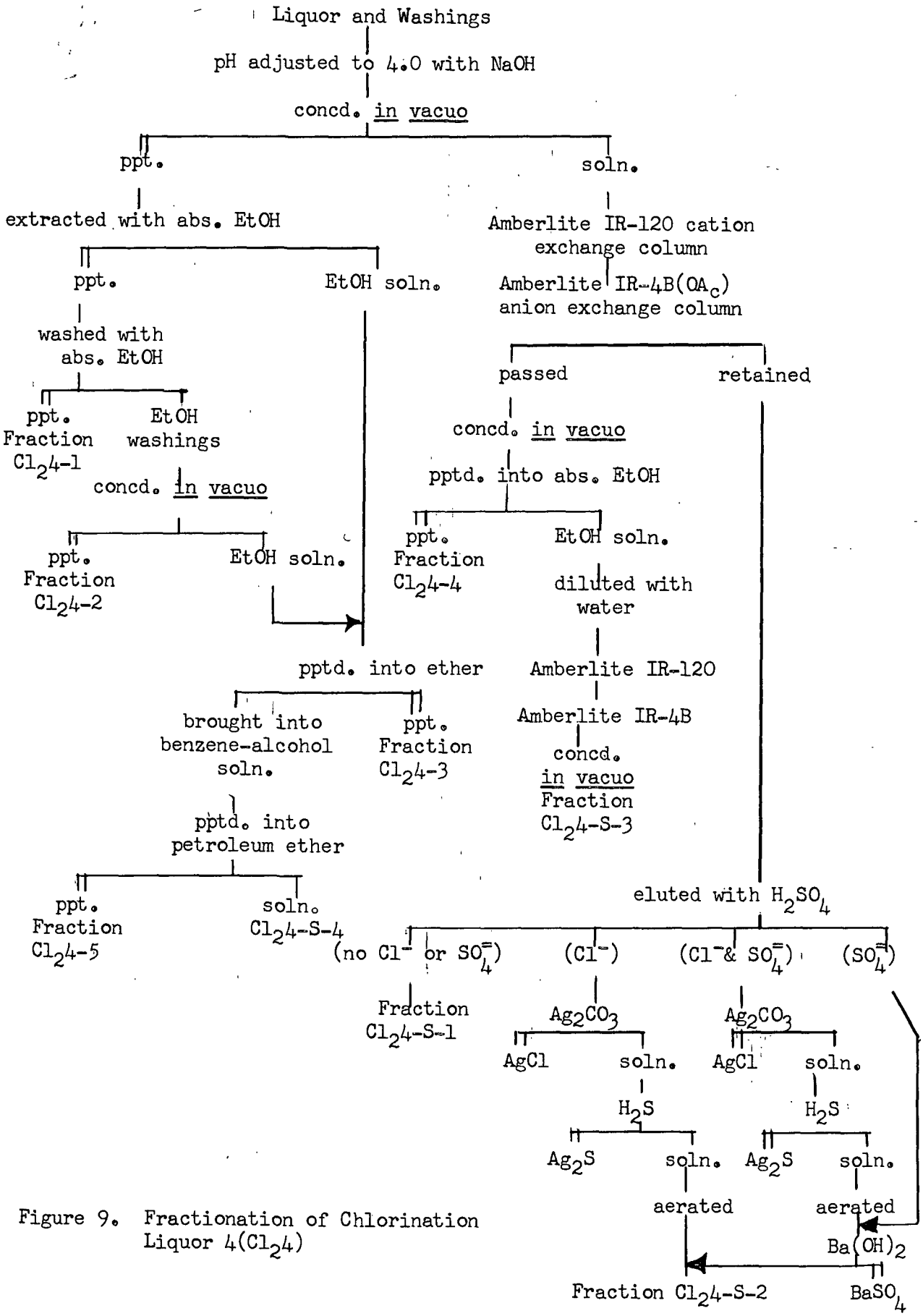

Figure 9. Fractionation of Chlorination Liquor 4(Cl_24)

The water solution was passed through an Amberlite IR-120 cation exchange column and an Amberlite IR-4B(OA_c^-) anion exchange column. The deionized solution was treated with five volumes of alcohol which yielded a precipitate containing carbohydrates. This was washed twice with ether and twice with low boiling petroleum ether and air dried (Fraction $Cl_2$4-4). The alcohol solution from this precipitation also contained carbohydrates. There were traces of free glucose or galactose, arabinose and xylose in the unhydrolyzed solution. After hydrolysis, the spots on chromatogram for these sugars were much more predominant.

The material retained by the anion column was eluted with sulfuric acid (pH = 1.0). The eluate was collected in four fractions as shown in Figure 9. Solution 1 which did not contain chloride or sulfate ions was concentrated in vacuo. The concentrated solution gave a negative Molisch test and was optically inactive. After hydrolysis, traces of xylose and galactose were indicated by a chromatogram. The chloride and sulfate ions were removed from the other three solutions which were then combined. These gave a positive Maule test and were optically inactive. The results of the Molisch test were uncertain. The solution was hydrolyzed with sulfuric acid (pH = 0.7). The sulfate ions were removed with barium hydroxide, and excess barium ions were removed on an Amberlite IR-120 cation exchange column. It was necessary to decolorize the solution with carbon to get a good separation on a paper chromatogram. The solution was chromatographed in the acid system. The presence of a trace material in the region between known mannose and arabinose spots was indicated after spraying with aniline hydrogen phthalate reagent. This spot was not found when the solution was chromatographed in the

pyridine system. When the solution was chromatographed in the acid system and sprayed with a 0.1% solution of p-sulfo-o-methoxybenzene-azodimethyl-α-naphthylamine, acids were indicated present at the starting line, in the region of a known mannose spot, and in the region of a known rhamnose spot. Another sample of the solution chromatographed in the acid system and sprayed with ferric-ferricyanide reagent indicated the presence of phenolic material at the starting line, in the region of a known galactose and glucose spot, in the region of a known arabinose spot and in the region of a known xylose spot.

The conclusion drawn from these observations was that acids were present in this fraction, small amounts of which may be carbohydrate in nature.

Data on the yield of the various fractions are given in Table XIX. The carbohydrate composition of the hydrolyzed liquor fractions expressed as percentage of the total material lost in chlorination is given in Table XX. There were no simple sugars in the unhydrolyzed fractions $Cl_2 4$-1 and $Cl_2 4$-4.

The total amount of sugars found in the hydrolyzates of the liquor fractions was 2.10% of the yield loss or 0.21% of the unbleached pulp.

FRACTIONATION OF THE LIQUORS FROM THE CAUSTIC-EXTRACTION STAGE

DEVELOPMENT OF THE SCHEME OF FRACTIONATION

The scheme of fractionation developed for the caustic-extraction liquors in the preliminary work is shown schematically in Figure 10. Data from this fractionation are given in Table XXI. The procedure, as

TABLE XIX

YIELDS OF LIQUOR FRACTIONS FROM CHLORINATION 4 ($Cl_2$4)

	Weight, g.	Yield Loss, %	"Maule" Test
Precipitated fractions			
$Cl_2$4-1	1.52[1]	5.0	pos.
$Cl_2$4-2	0.06	0.2	?
$Cl_2$4-3	5.84	19.2	pos.
$Cl_2$4-4	1.00	3.3	?
$Cl_2$4-5	5.30	17.4	pos.
Soluble fractions			
$Cl_2$4-S-1	0.53[2]	1.7	
$Cl_2$4-S-2	1.32	4.3	
$Cl_2$4-S-3	0.60	2.0	
$Cl_2$4-S-4	1.06	3.5	
Washings			
From fraction 2	0.02	0.1	
From fraction 3	0.01	0.03	
From fraction 4	0.01	0.03	
		56.8[3]	

[1] Ovendry, ash-free weight

[2] Ovendry solids

[3] See page 77 for discussion

TABLE XX

CARBOHYDRATE COMPOSITION OF THE LIQUOR FRACTIONS OF CHLORINATION $4(Cl_24)$[1]

	Galactan, %	Glucan, %	Mannan, %	Araban, %	Xylan, %	Rhamnan, %
Cl_24-1	0.23	0.03	--	0.35	0.23	--
Cl_24-2	--	--	--	Trace?	--	--
Cl_24-3	--	--	--	Trace?	--	--
Cl_24-4	0.20	0.02	Trace?	0.22	0.41	0.03
Cl_24-5	--	--	--	--	--	--
Cl_24-S-1	Trace	Trace	--	--	Trace	--
Cl_24-S-2	Trace	--	--	--	--	--
Cl_24-S-3	0.01	0.06	--	0.20	0.01	--
Total	0.44	0.11	Trace?	0.87	0.65	0.03

[1] Expressed as the percentage of the pulp yield loss in chlorination.

TABLE XXI

DATA FROM THE FRACTIONATION OF
CAUSTIC-EXTRACTION LIQUOR 4(C.E.4)

	Weight[1] g.	% of Chlorinated Pulp Yield Loss	Maule Test	Molisch Test
Precipitated fractions				
C.E.4-1	1.21	23.7	pos.	neg.
C.E.4-2	0.59	11.5	pos.	pos.
C.E.4-3	0.15	2.9	?	pos.
C.E.4-4	0.18	3.6	?	pos.
C.E.4-5	1.22	23.8		
Soluble fractions				
C.E.4-S-1	1.33	26.2	Not tested	
C.E.4-S-2	0.57	10.2	pos.	?
C.E.4-S-3	0.59	11.5	Not tested	
		113.4%		

[1] Airdry weight, uncorrected for ash

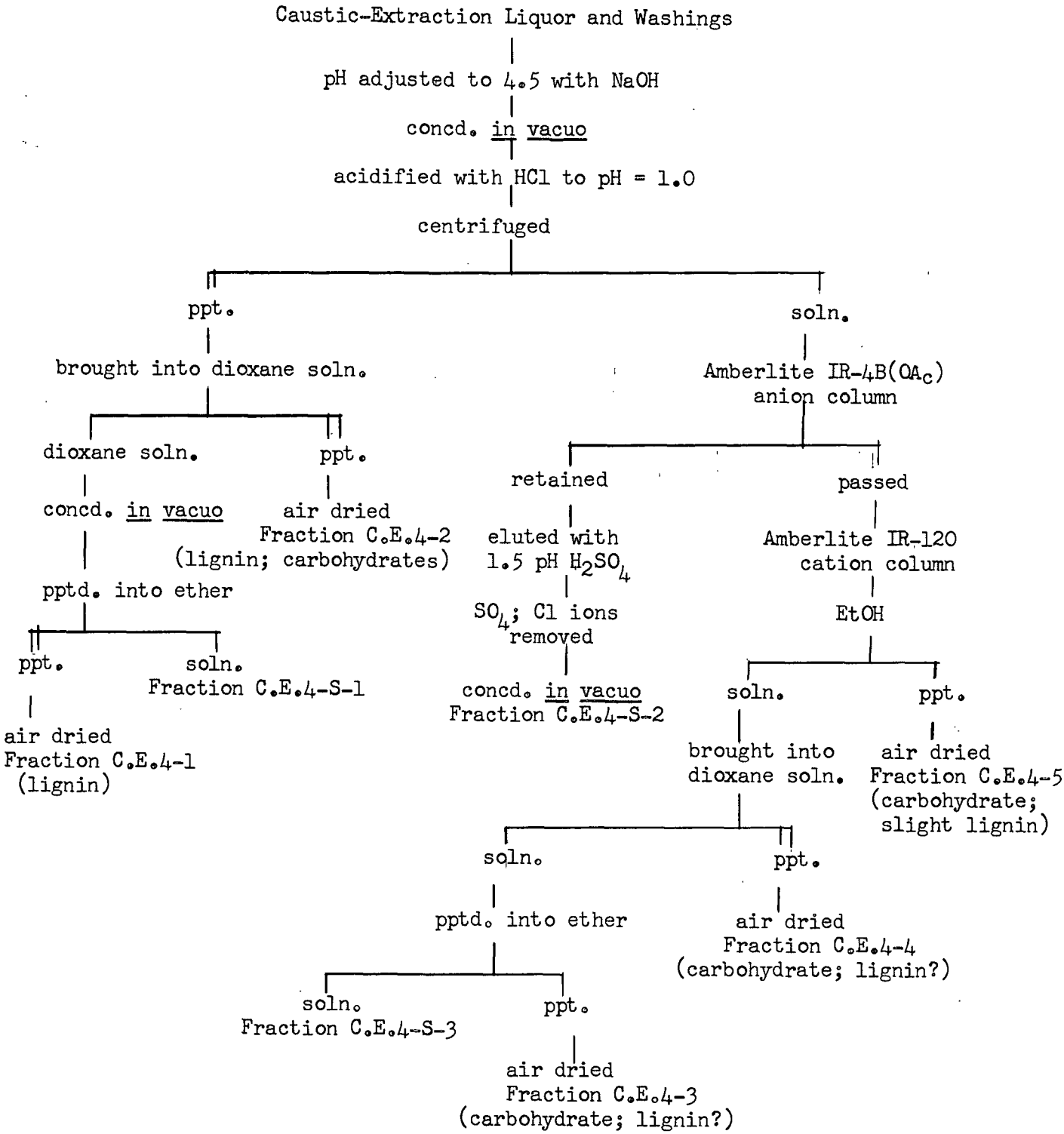

Figure 10. Scheme of Analysis for Caustic-Extraction Liquor 4 (CE4)

finally adopted, will be discussed in detail in the following section on the quantitative fractionation.

Another scheme of fractionation had been developed in which the sodium ions were first removed batchwise by a cation resin and then the main separation was achieved by precipitating with alcohol. This was discarded since material could have precipitated on the cation resin due to the change in pH.

QUANTITATIVE FRACTIONATION

The liquors from caustic extraction 5 were used in the quantitative study. The details of the fractionation are shown schematically in Figure 11.

The liquors and wash water from caustic extraction 5 were acidified immediately to a pH of 4.0 with hydrochloric acid and then filtered through a double layer of Cenco No. 13260 filter paper. The liquor was concentrated in vacuo from a volume of 28 liters to about 1 liter. The pH of the concentrated liquor was adjusted to 1.0 with hydrochloric acid and at that pH, the precipitation of acid-insoluble material was complete. The precipitate was separated by centrifuging. This precipitate is an acid-insoluble material and not matter simply thrown down because of a high salt concentration. A small portion of the precipitate was resuspended in water six times and each time it could be precipitated with hydrochloric acid.

The acid solution was passed immediately through an Amberlite IR-4B (OA_c) anion column. The effluent from the anion column was immediately

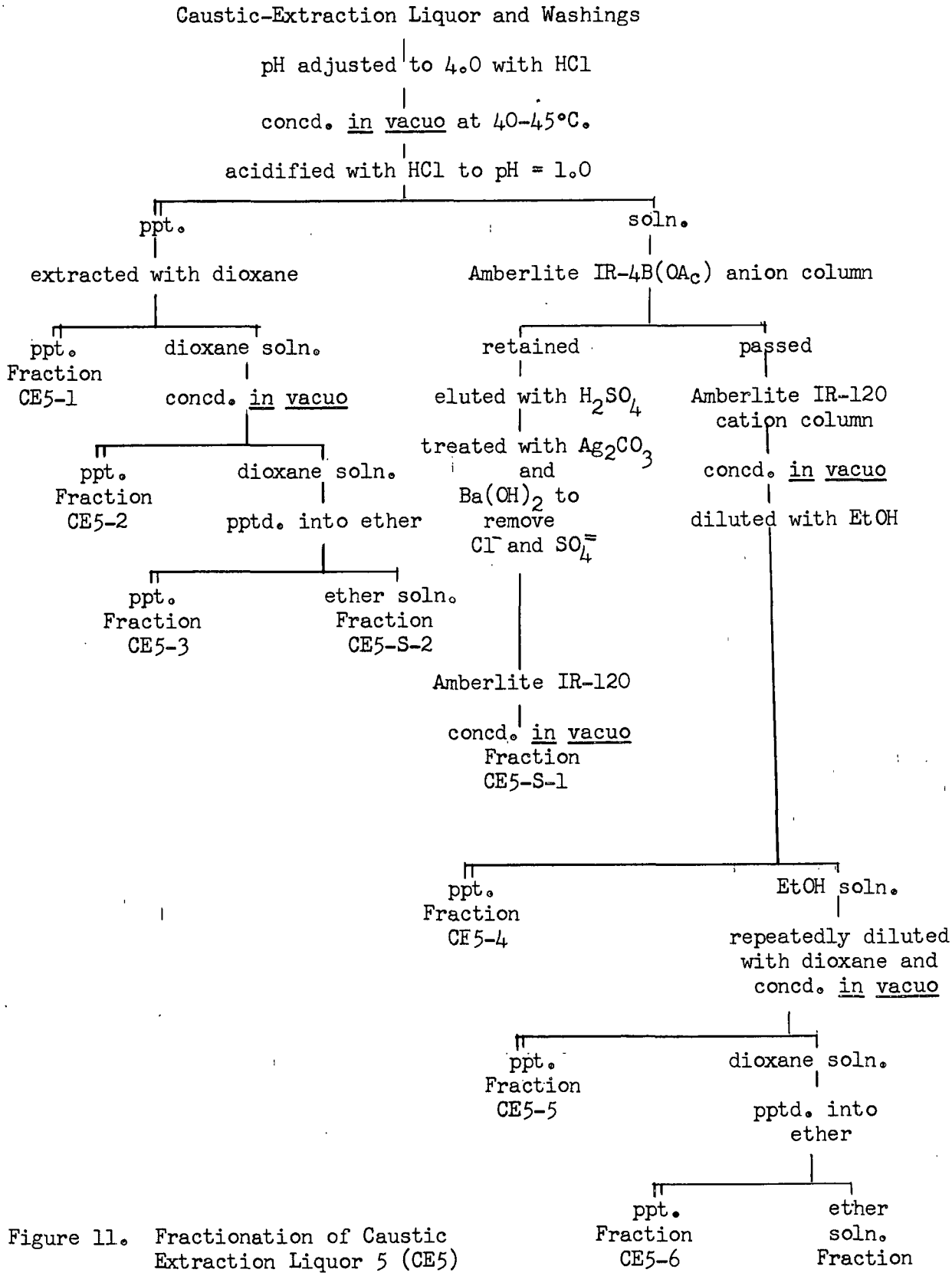

Figure 11. Fractionation of Caustic Extraction Liquor 5 (CE5)

passed through an Amberlite IR-120 cation column. The effluent from the cation column was concentrated in vacuo and poured into five volumes of ethyl alcohol. Only a slight precipitate formed. The mixture was diluted repeatedly with absolute alcohol and concentrated in vacuo until no further precipitation occurred. The precipitate was washed twice with ether and twice with low boiling petroleum ether and then air dried (Fraction CE504).

The alcohol solution was diluted repeatedly with purified dioxane and concentrated in vacuo until no further precipitation occurred. The precipitate was washed twice with ether and twice with low boiling petroleum ether and then air dried (Fraction CE5-5). The dioxane solution when poured dropwise into ether gave a precipitate which was washed twice with ether and twice with low boiling petroleum ether and then air dried (Fraction CE5-6).

The anion exchange column was eluted with sulfuric acid (pH = 1.5). The chloride ions in the eluate were precipitated with silver carbonate and the sulfate ions were precipitated with barium hydroxide. Any excess silver or barium ions were removed by passing the solution through an Amberlite IR-120 cation column. The solution, which was never allowed to become basic, was concentrated in vacuo at 40-45°C. (Fraction CE5-S-1).

The acid-insoluble material was extracted with purified dioxane by repeatedly suspending the wet precipitate in dioxane and concentrating in vacuo until further dioxane extractions were colorless. The dioxane-insoluble material was washed twice with ether and twice with low boiling petroleum ether and air dried (Fraction CE5-1).

The combined dioxane extracts were concentrated *in vacuo*. A small amount of material which precipitated was washed with ether, petroleum ether and air dried (Fraction CE5-2).

The concentrated dioxane solution was poured dropwise into ether, and the resulting precipitate was washed twice with ether and twice with petroleum ether and then air dried (Fraction CE5-3).

Data on yields of the liquor fractions are given in Table XXII. The carbohydrate composition of the liquor fraction after hydrolysis is given in Table XXIII. The unhydrolyzed fraction CE5-1 contained traces of arabinose, xylose and xylobiose. The unhydrolyzed fractions CE5-2, CE5-3, and CE5-4 contained traces of arabinose.

The total amount of sugars found in the hydrolyzates of the liquor fractions was 10.36% of the yield loss resulting from caustic extraction. This was 0.44% of the chlorinated pulp or 0.39% of the original unbleached pulp.

TABLE XXII

YIELDS OF THE LIQUOR FRACTIONS FROM CAUSTIC EXTRACTION 5 (CE5)

	Weight, g.	% of Yield Loss	Maule Test
Precipitated fractions			
CE5-1	1.4430	9.63	slight
CE5-2	1.2100	8.07	pos.
CE5-3	5.1236	34.20	pos.
CE5-4	0.8966	5.97	slight
CE5-5	0.0605	0.40	pos.
CE5-6	0.3289	2.19	pos.
Solutions			
CE5-S-2	3.40	22.64	
CE5-S-1	1.28	8.50	
Washings			
From CE5-1	0.19	1.25	
From CE5-2	0.07	0.47	
From CE5-4	0.01	0.01	
From CE5-5	0.19	1.25	
From CE5-6	0.91	6.04	
		100.62%	

TABLE XXIII

CARBOHYDRATE COMPOSITION OF THE LIQUOR FRACTIONS FROM CAUSTIC EXTRACTION 5 (CE5)

	Galactan, %	Glucan, %	Mannan, %	Araban, %	Xylan, %	Rhamnan, %
CE5-1	0.49	0.06	--	0.19	4.29	0.03
CE5-2	0.44	0.02	--	0.49	0.17	0.03
CE5-3	--	--	--	0.19	--	--
CE5-4	0.37	0.09	Trace?	0.55	2.52	0.06
CE5-5	Trace	Trace	Trace?	Trace	Trace	Trace?
CE5-6	Trace	Trace	--	Trace	Trace	--
CE5-S-1	--	--	--	0.32	0.05	--
Total	1.30	0.17	--	1.74	7.03	0.12

[1] Polysaccharide expressed as percentage of yield loss in caustic extraction.

DISCUSSION OF RESULTS

SUMMARY OF DATA

The results of the analysis of the pulp residues and of the bleach liquors are summarized in Tables XXIV and XXV. It is possible to calculate various fractions of the pulp using data from independent determinations and obtain good precision. This adds credibility to the individual determinations. The results of such manipulations of data are shown in Table XXVI.

The sum of the pentosans and polyuronides in the pulp residues as determined by standard methods is equal to the sum of these components in the alkali-resistant cellulose and hemicelluloses. The pentosans (xylan) in the alkali-resistant cellulose was determined by paper chromatography. (No uronic acid material was indicated in this fraction). The polyuronides and pentosans in the hemicelluloses were calculated by subtracting the amount of hexosans (galactan) as determined again by paper chromatography from the total weight of the hemicellulose.

The sum of the pentosan sugars in the alkali-resistant cellulose and hemicelluloses as determined by paper chromatography is essentially the same as the pentosans as determined by the standard method for the unbleached and chlorinated pulps. The precision was not as good for the caustic-extracted pulp. Discrepancies in this particular balance could be due to the difficulty in hydrolyzing aldobiuronic acids which bind xylose units, that would not appear as xylose in a chromatogram (Refer to Table XV).

TABLE XXIV

SUMMARY OF PULP ANALYSIS DATA

Basis--100 g. Ovendry Ash-free Unbleached Pulp

	Unbleached Pulp	Chlorinated Pulp	Caustic-Extracted Pulp
Yield, g.	100.0	90.6	85.7
Alcohol soluble, g.	1.2	5.4	0.7
Klason lignin, g.	10.0	2.5	2.0
Soluble lignin, g.	4.6[1] 3.5[2]	2.0[1] 0.4[2]	1.6[1] 0.3[2]
Holocellulose,[3] g.	85.2	84.5	83.3
Alkali-resistant cellulose, g.	63.3	63.5	63.1
Hemicellulose, g.	20.5	20.4	19.7
Pentosans,[4] g.	17.9	18.0	17.7
Polyuronides, g.	3.88	3.70	3.51

[1] Calculated using Equation (1) at 230 mmu

[2] Calculated using Equations (2) and (3)

[3] Uncorrected for ethanolamine

[4] Corrected for uronic acids

TABLE XXV

SUMMARY OF LIQUOR ANALYSIS DATA

Basis--100 g. Ovendry Ash-free, Unbleached Pulp

	Chlorination Liquor 4	Caustic-Extraction Liquor 5
Total amount of material lost, g.	10.1	3.5
Total amount of material recovered, g.	5.7	3.5
Recovery, %	56.8	100.6
Total amount of noncarbohydrate material recovered, g.	5.5	3.1
Total amount of carbohydrate material recovered, g.	0.21	0.39
Amount of individual sugars recovered, g.		
a. galactan	0.05	0.05
b. glucan	0.006	0.01
c. mannan	Trace ?	Trace?
d. araban	0.09	0.06
e. xylan	0.06	0.25
f. rhamnan	Trace	0.01

TABLE XXVI

CARBOHYDRATES FRACTION BALANCES AND SUMMATIVE ANALYSES[3]

	Unbleached Pulp	Chlorinated Pulp	Caustic-Extracted Pulp
Pentosan + polyuronides	21.8	21.7	21.2
Hemicellulose--galactan in hemicellulose + xylan in alkali-resistant cellulose	21.9	21.8	20.9
Pentosans	17.9	18.0	17.7
Xylan + araban in hemicellulose + xylan in alkali-resistant cellulose	18.0	17.7	16.9
Holocellulose corrected for nitrogen as ethanolamine	84.1	83.7	82.6
Alkali-resistant cellulose + hemicellulose	83.8	83.9	82.8
Yield	100.0	90.6	85.7
Yield by summative analysis			
A[1]	99.6	93.8	87.1
B[2]	98.5	92.2	85.8

[1] Soluble lignin calculated using Equation (1) at 230 mmu.

[2] Soluble lignin calculated using Equations (2) and (3).

[3] Expressed as percentage of unbleached pulp.

The value for holocellulose, after correcting for all the nitrogen as ethanolamine, is closely approximated by the sum of its components, i.e., alkali-resistant cellulose and hemicelluloses.

A good summative analysis was obtained for the unbleached and caustic-extracted pulps. The components included in the summative analysis were the alkali-resistant cellulose, hemicelluloses, Klason lignin, soluble lignin and alcohol extractives. The high value for the summation of these components for the chlorinated pulp was probably caused by errors in the lignin determination. This is discussed further on page 82.

THE LOSS OF CARBOHYDRATE MATERIAL IN THE CHLORINATION STAGE

The total loss of carbohydrate material during chlorination was shown by both pulp and liquor analysis to be exceedingly small. As measured by the analysis of pulp residues, the loss was within the experimental error of the methods. Measurement of the simple sugar content of the spent liquor fractions after hydrolysis indicated a loss of only 0.2% on the unbleached pulp basis.

The results of the analysis of the pulp residues demonstrated that there was no change in the absolute amount of either the alkali-resistant cellulose or the hemicelluloses. Analysis of the hydrolyzates of these two fractions indicated no change in the composition of the alkali-resistant cellulose, but did indicate, possibly, a small loss of galactan and araban in the hemicelluloses. There was no change in the pentosan content. A slight change may have occurred in the uronic acid content as measured by carbon dioxide evolution (0.18% of the unbleached pulp).

Based on pulp yields, about 10% of the unbleached pulp was lost during chlorination. The pulp analysis indicated that this was essentially all noncarbohydrate material, presumably lignin. By the methods of spent liquor analysis, about 57% was recovered; 55% was noncarbohydrate material and 2% was carbohydrate material as indicated by the amount of simple sugars found after hydrolysis.

The presence of only small amounts of carbohydrates in the spent liquor is in agreement with the results of the pulp analysis. It is believed that all carbohydrate material in the spent liquor (simple sugars and material which yielded simple sugars on hydrolysis) was recovered. The only such material which may have been lost would have been water-soluble, acidic carbohydrates. These may have precipitated when the acidic part of the water-soluble fraction, after being isolated by means of the anion exchange column, were treated with silver carbonate and barium hydroxide (Fractions $Cl_2$4-S-1 and $Cl_2$3-S-2). It was demonstrated in the preliminary work that the water-soluble fraction yielded only xylose and arabinose with a trace of galactose on hydrolysis. Since the results of the pulp analysis indicated no change in either the pentosans or the hemicellulose, the loss of carbohydrate material in this manner must have been small.

Uronic acid material was qualitatively indicated in the spent liquor. It was not quantitatively determined. However, again the pulp analysis data showed the loss of uronic acids was small.

No attempt was made to determine carbohydrate oxidation products from chlorination. Such a study would be a complex problem in itself

because the methods for dealing with such materials are still in the beginning stages of development. However, since the yield and composition of the carbohydrate fraction of the pulp was demonstrated to be essentially unchanged by chlorination, it appears that the oxidation of carbohydrates in the chlorination studied was very limited. This would be expected since the work of Dyfverman, Lindberg and Wood (6), Lindberg and Wood (7), and Dyfverman (8), indicated that the oxidation reaction of carbohydrates by chlorine under the conditions of commercial chlorination of wood pulps would be extremely slow.

Although it is believed that all of the carbohydrates lost in chlorination were accounted for by the method of spent liquor analysis, noncarbohydrate products could have been lost. Considerable amounts of acidic lignin material in Fractions Cl_24-S-1 and Cl_24-S-2 could have precipitated as silver or barium salts. Also, noncarbohydrates may have been lost as volatiles during the initial concentration of the liquor from 40 liters to 160 ml. and in the measurement of the solids concentration of the several soluble fractions, for example, Fraction Cl_24-S-4. These soluble fractions gave off strong odors and continued to lose weight on protracted drying in vacuo. Since only traces of simple sugars were found in the unhydrolyzed liquor fractions, it was concluded that the sugars determined in the hydrolyzates of these fractions were those removed from the pulp. The predominant sugars found were galactose, arabinose, and xylose with traces of glucose, mannose, and rhamnose.

The loss of carbohydrates in chlorination was not necessarily caused by the action of the chlorine alone but as previously shown, it probably

was caused by the combined action of water, agitation, and chlorine. Merely soaking the pulp in cold water caused the removal of 0.2% material which contained the same carbohydrates as removed by chlorination. The amount of this material removed increased with the degree of agitation. The degree of agitation also seemed to have a strong effect on the character of the chlorinated pulp residues because with vigorous agitation during the chlorination, the pulp became very mushy.

The analysis of the hydrolyzates from the hemicelluloses indicated that the carbohydrates removed in the chlorination stage may have come from the analytically-defined hemicellulose fraction. Whatever the source, they probably represent an easily removable fraction. Such a group of easily removable carbohydrates could result from the air drying and storage of unbleached pulp. They could also be degradation products from the pulping operation which were not completely removed in washing the unbleached pulp.

It is also possible that these carbohydrates were chemically combined with lignin and were rendered soluble after being split from lignin during chlorination or were removed directly with lignin. The difficulty encountered in attempting to separate the carbohydrates and lignin in fraction $Cl_2$4-1 indicates the possibility that some of the carbohydrates removed may have been combined with lignin. It is interesting to note that Traynard and Ayroud (23) found that galactose, arabinose, and xylose contaminated various lignin fractions isolated from aspenwood after extensive purification designed to eliminate free carbohydrates.

The resistance of the carbohydrate fraction to chlorination may be explained in part by the rapid consumption of chlorine by the pulp (probably by substitution in lignin as demonstrated by Giertz (25), Voigtman (26) and Larson (3). In less than two minutes, 80% of the chlorine was consumed, leaving a concentration of 0.7 g./l. active chlorine. In five minutes this was reduced further to less than 0.3 g./l.

THE LOSS OF CARBOHYDRATE MATERIAL IN THE CAUSTIC-EXTRACTION STAGE

The total amount of carbohydrate material removed by caustic extraction of the chlorinated pulp was also shown to be very small. The results of the pulp analysis indicated that about 1% carbohydrates on the unbleached pulp basis was lost. A small change occurred in the absolute amounts of hemicelluloses and uronic acids but only a slight change occurred in the amounts of alkali-resistant cellulose and pentosans. Analysis of the hydrolyzates from the alkali-resistant celluloses indicated a slight loss of xylan and analysis of the hydrolyzates from the hemicelluloses indicated a slight loss of galactan and araban, but these losses were within experimental error.

In the spent liquor, about 0.4% of material on the unbleached pulp basis was found which yielded simple sugars on hydrolysis. Uronic acid material was also qualitatively detected. Most of the sugar units found were xylose, indicating that probably the hemicellulose fraction was attacked in the reaction. Small traces of galactose, glucose, mannose, and rhamnose were also found after hydrolysis. Only trace amount of these units were present as simple sugars before hydrolysis.

About 4% of material on the unbleached pulp basis was lost during caustic extraction as determined by the pulp yields. The method of liquor analysis accounted for 100% of this loss. About one-tenth was found to yield simple sugars on hydrolysis.

Although the temperature of the caustic-extraction stage was 50°C., the concentration of alkali was low. Two per cent sodium hydroxide on the ovendry pulp basis was used which is only a 0.2% solution. At the end of the extraction less than one-fourth of the initial alkali remained thus indicating that most of the original alkali was consumed by the acids in the chlorinated pulp. The final pH was 9.3. This relatively gentle treatment may, in part, account for the limited attack on the carbohydrates particularly in view of the alkalinity and high temperature of the pulping conditions. The initial pH of the pulping liquors was 11.3; that of the caustic extraction liquors was 12.4.

THE LOSS OF LIGNIN MATERIAL IN THE CHLORINATION AND CAUSTIC-EXTRACTION STAGES

Errors and uncertainties make it difficult to use the values of the Klason and soluble lignin contents of the pulp residues in studying the effectiveness of the two bleaching stages for lignin removal. A serious error in the determination of Klason lignin was the loss of appreciable amounts of lignin in the chlorinated pulp by solution during the 95% ethyl alcohol preextraction. The extract gave a positive Mäule test which was not true for the alcohol extracts of the unbleached and caustic-extracted pulps. It also contained the simple sugars, xylose, and arabinose. The presence of carbohydrates in this extract may have

caused the summative analysis of the chlorinated pulp to be high (Table XXVI). The Klason lignins were not corrected for changes in sulfur or chlorine contents. A correction for the chlorine content might have been particularly significant. Since, however, the corrections were not made, the summative analysis of the chlorinated and caustic-extracted pulp may have been high.

Since the total loss of extractives through both bleaching stages as measured by the alcohol-soluble content was small, the loss of noncarbohydrate material should be a reasonable estimate of lignin losses. If the noncarbohydrate fraction is calculated as the difference between the pulp yield and the sum of the alkali-resistant cellulose and hemicelluloses, it would be 16.2% for the unbleached pulp, 6.7% for the chlorinated pulp, and 2.5% for the caustic-extracted pulp (unbleached pulp basis). Then, the loss of lignin in terms of unbleached pulp would be 9.5% by chlorination and 4.2% by caustic extraction. These figures agree with the removal of noncarbohydrate material as indicated by the liquor analysis.

It appears, then, that both stages are significantly effective in removing lignin. In commercial practice where the chlorinated pulp is not as thoroughly washed, the caustic-extraction stage may account for a greater ratio of the total material removed. It was demonstrated that the washings from the chlorinated pulp contain more material than did the original chlorination liquor. As the washing continued and the pH rose, probably more material became soluble than that in the acid system of the chlorination liquor.

The large amounts of material in spent liquors from chlorination and caustic extraction which were soluble in ether and petroleum ether suggest that the lignin may have been extensively degraded in these bleaching operations.

SUMMARY AND CONCLUSIONS

1. The loss of carbohydrate material during chlorination was found to be exceedingly small. In the spent liquors, 0.2% of carbohydrate material on the unbleached pulp basis was found which yielded mainly galactose, arabinose, and xylose after hydrolysis. Only a small portion of these was detected as simple sugars prior to hydrolysis. Uronic acids were also qualitatively indicated in the spent liquor. Analysis of the pulp residues indicated a loss of 0.2% polyuronides (unbleached pulp basis).

The loss of carbohydrates during chlorination could have resulted from a combination of the following circumstances:

a. Degradation products from cooking which were not completely removed in washing the pulp or from air drying and storing the pulp, may have dissolved during chlorination. It was demonstrated that water and agitation alone could remove carbohydrate material of similar composition.

b. There may have been a slight attack on the hemicelluloses as evidenced by a slight change in their simple sugar composition after chlorination.

c. There may have been some carbohydrates chemically linked with lignin as evidenced by the difficulty in separating lignin and carbohydrates in one of the spent liquor fractions.

The limited attack on the carbohydrate fraction was probably due to the extremely rapid consumption of chlorine by pulp (probably by substitution in lignin).

2. The loss of carbohydrate material during caustic extraction was found to be small. In the spent liquors, about 0.4% of carbohydrate material (on the unbleached pulp basis) which consisted mainly of xylose with smaller amounts of galactose and arabinose was found in the spent liquor. Only a small portion of these were simple sugars in the unhydrolyzed state. Analysis of the pulp residues indicated a small loss of hemicelluloses (0.7% on the unbleached pulp basis). Of this, about 0.2% was found to be uronic acids.

Based on the results of the spent liquor and pulp analysis, there appears to be a mild attack on the hemicelluloses.

The limited attack on the carbohydrate fraction during caustic extraction may be due to the fact that the pulping conditions were alkaline and the fact that the extraction stage is relatively gentle. The initial alkali concentration is low and is further reduced by acidic material on the chlorinated pulp.

3. Both chlorination and caustic extraction were significantly effective in removing lignin. Assuming the noncarbohydrate fraction to be mainly lignin, it was found that chlorination removed 9.5% lignin and caustic extraction removed 4.2% (unbleached pulp basis). The total lignin in the unbleached pulp was 16.2%. The amount of material removed by chlorination depended on the degree of washing because as the pH of the washings approached 7 (the pH of initial chlorination liquor was 1.3) considerable amounts of material were removed.

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